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De Beers Technology UK

434

INTERNATIONAL GEMOLOGICAL INSTITUTE

LABORATORY GROWN DIAMOND REPORT

Report Number: LG10061905

DATE: 4/27/2011

DESCRIPTION: LABORATORY GROWN DIAMOND

SHAPE AND CUTTING STYLE: ROUND BRILLIANT CUT

MEASUREMENTS: 4.78 x 4.93 x 2.93 mm

DIAMOND INFO:

Carat Weight: 0.94 CT

Color Grade: F

Clarity Grade: VS2

Cut Grade: EXCEL

PROPORTIONS:

Depth: 61.9%

Table: 97%

Crown Height % - Ang: 14.0% - 33.0°

Pavilion Depth % - Ang: 44.0% - 41.0°

Girdle: THIN TO MEDIUM

Culet: NONE

FINISH:

Polish: VERY GOOD

Symmetry: VERY GOOD

FLUORESCENCE: NONE

COMMENT: GIRDLE LASERSCRIBED "GEMESIS CREATED LG10061905"

THE LABORATORY GROWN DIAMOND DESCRIBED ABOVE IS CLASSIFIED AS A TYPE IIA.

PHOTO ENLARGED

COLOR GRADING SCALE: CL (Colorless) to K (Faint Yellow)

CLARITY (GR) GRADING SCALE: FL (Flawless) to I2 (Included)

The laboratory grown diamond described in this Report ('Report') has been graded, tested, analysed, examined and/or inscribed by International Gemological Institute (I.G.I.). A laboratory grown diamond is one that has the same chemical, physical and optical properties as mined diamond, with the exception of being grown by man. I.G.I. employs and utilizes those techniques and equipment currently available to I.G.I., including, without limitation, 10X magnification, corrected triplet loupe and binocular microscopy, master color comparison system, non-contact-optical measuring device, and such other instruments and/or processes as deemed appropriate by I.G.I. This Report includes advanced security features. A duly accredited gemologist or jeweler can advise you with respect to the importance of and interrelationship between cut, color, clarity and carat weight.

THE REPORT IS ISSUED AS A GUARANTEE, VALIDATION AND APPROVAL OF THE LABORATORY GROWN DIAMOND DESCRIBED HEREIN.

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Figure 3: Scanned copy of the IGI certificate that was included with the Gemesis sample

On the Gemesis invoice, the following declaration was present: "Disclosure: All diamonds from Gemesis are lab-created, guaranteeing a socially and ecologically responsible point of origin."

The IGI report specifies that the dimensions of the round brilliant are 4.78 mm x 4.93 mm x 2.93 mm.

The IGI report gives the description 'Laboratory Grown Diamond' and includes the comment: "Girdle laserscribed 'Gemesis Created LG10061905'". The report contains the following statement: "The laboratory grown diamond described in this Report ('Report') has been graded, tested, analysed, examined and/or inscribed by International Gemological Institute (I.G.I.). A laboratory grown diamond is one that has the same chemical, physical and optical properties as mined diamond, with the exception of being grown by man. I.G.I. employs and utilizes those techniques and equipment currently available to I.G.I., including, without limitation, 10X magnification, corrected triplet loupe and binocular microscopy, master color comparison system, non-contact-optical measuring device, and such other instruments and/or processes as deemed appropriate by I.G.I. This Report includes advanced security features. A duly accredited gemologist or jeweler can advise you with respect to the importance of and interrelationship between cut, color, clarity and carat weight."

RESULTS

3.1 Microscopy and birefringence images

Microscopy images were recorded (please see Figure 4). The gemstones were of good colour and cut but inclusions were visible and can be seen in the images in Figure 4.

The stone possessed a girdle inscription which was straightforward to locate and contained the words 'GEMESIS CREATED' followed by letter / number combination that correlated with the IGI certificate numbers. One of the images in Figure 4 shows the inscription.

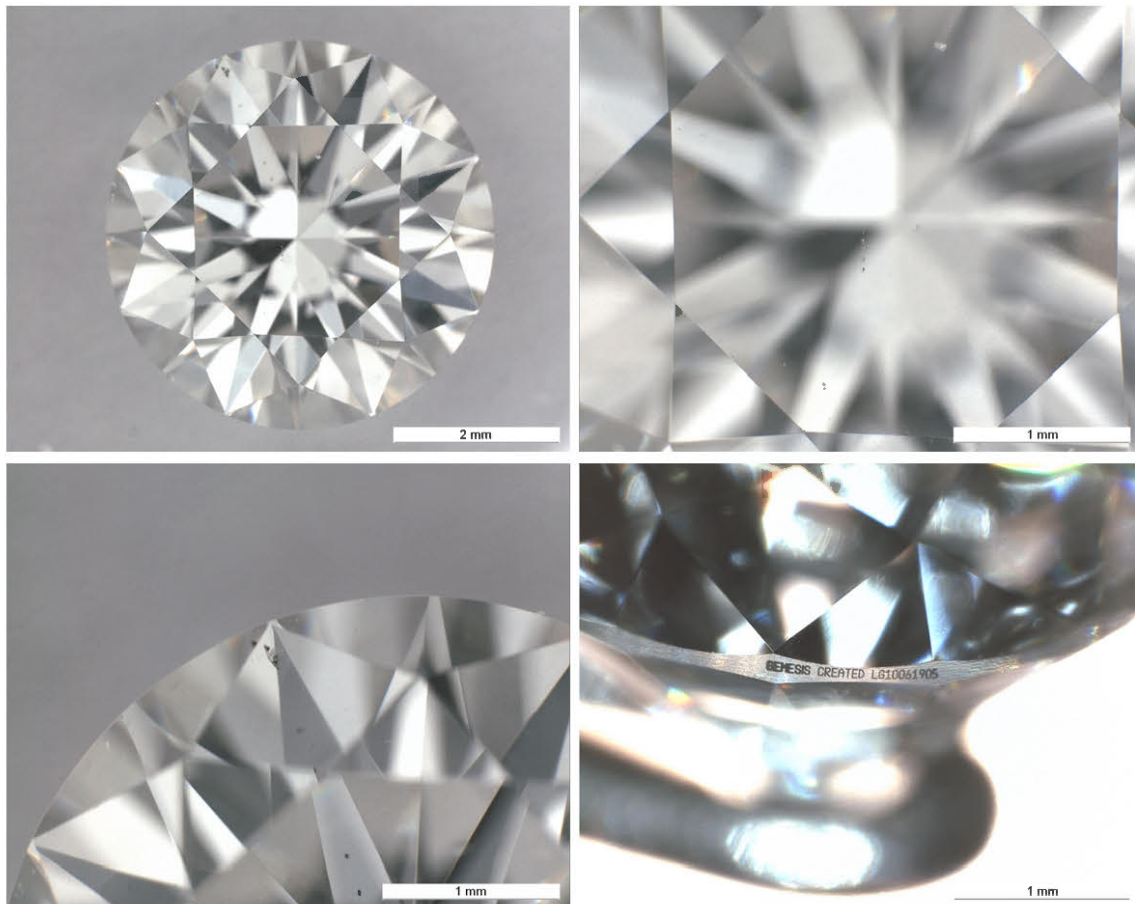


Figure 4: Microscopy images for the Gemesis stone NL530, showing inclusions and the girdle inscription

3.2 DiamondSure and DiamondPLus

NL530 was tested using DiamondSure and DiamondPLus, instruments developed by De Beers Technologies and now sold by IIDGR. The results are shown in Table 2. DiamondPLus gave an average 737 nm Raman-normalised photoluminescence intensity value of 0.454. DiamondPLus uses 658 nm laser diode to excite this luminescence feature at 737 nm with the sample immersed in liquid nitrogen. The 737 nm photoluminescence line is commonly detected for CVD synthetic diamond.

Gemstone	DiamondSure results	DiamondPLUS results
NL530	'Refer for further tests (Type II)'	'Refer (CVD synthetic?) 737nm'

Table 2: DiamondSure and DiamondPLus results for the NL530 stone

3.3 DiamondView images

DiamondView fluorescence and phosphorescence images were recorded (Figure 5). NL530 exhibited bluish-green fluorescence and blue phosphorescence, a combination that we have commonly observed for nitrogen-doped CVD synthetics that have been high-temperature treated (between 1800 and 2300°C). Such a heat treatment is likely to have been performed to remove brown coloration, and as a consequence of the heat treatment the dominant colour of the fluorescence has been changed from the orange colour typical of as-grown nitrogen doped CVD synthetic diamond, to the observed bluish-green colour.

DiamondView fluorescence images of the sample show obvious striations that are indicative of differential uptake of defects on the risers and terraces of growth steps that were formed during the CVD diamond synthesis process. The presence of these striations provides evidence that the gemstones are CVD synthetic in origin.

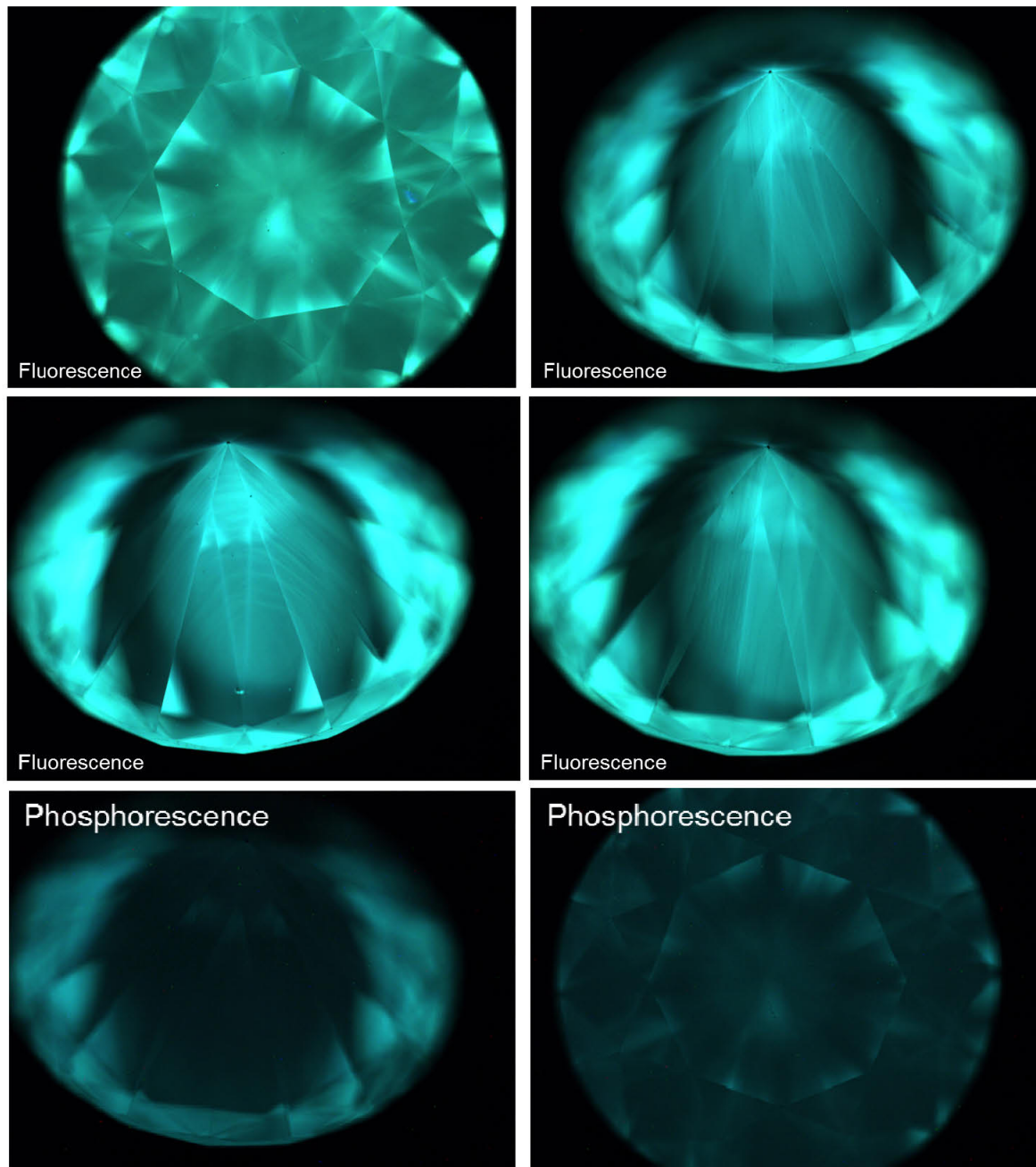
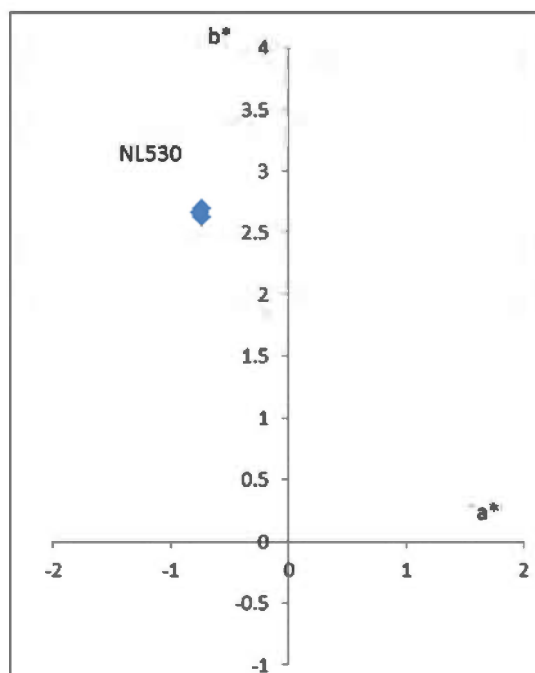


Figure 5: DiamondView fluorescence and phosphorescence images for NL530

3.4 Polished colour measurement

We used the Falcon colour measurement system to deduce L^* , a^* and b^* colour coordinates for NL530 and assign a colour grade. Three measurements were taken. The results, as shown in Figure 6, lie in the upper-left b^*a^* quadrant (i.e. negative a^* values), consistent with a yellow hue. As-grown (unannealed) nitrogen-doped CVD synthetics possess some degree of brown colour, which would lead to positive a^* values. After heat treatment to remove the brown colour, a yellow hue remains, which is due to neutral single substitutional nitrogen (N_S^0) impurities. This is a further indication that these gemstones have been heat-treated.

Using Falcon, a colour grade of F was deduced, with the subgrade 3 indicating that the colour was not far from the centre of this grade (Table 3). This colour grade is in agreement with the IGI's colour grading result.



	IGI grade	Falcon grade
NL530	F	F3

	L^*	a^*	b^*	c^*	Grade
NL530	96.28	-0.75	2.66	2.77	F3

*Figure 6: b^*a^* colour coordinates for NL530 gemstones, as deduced using the Falcon polished colour system.*

*Table 3: $L^*a^*b^*c^*$ values for NL530 as deduced using Falcon.*

3.5 Infrared spectroscopy

Prior to measurement, the sample was exposed to ~5 minutes UV radiation using a DiamondView instrument in order to stabilise the charge states of the defects. Infrared spectra were then recorded for NL530 using a ThermoFisher Nicolet 380 FTIR spectrometer in diffuse reflectance mode. The spectrum was obtained using 0.5 cm^{-1} resolution, 512 scans and, after the measurement, a water spectrum was subtracted from the sample spectrum. Absorption coefficient values were deduced by multiplying the data points by a factor that was calculated by dividing 11.95 by the absorbance at 1995 cm^{-1} . The spectrum is shown in Figure 7. It contains very little absorption apart from the intrinsic absorption of diamond. The 1332 cm^{-1} peak indicates an upper limit for N_s^+ of 0.11 ppm but the concentration of single substitutional nitrogen was low enough for no peak to be observed at 1344 cm^{-1} and this is consistent with the good colour grade (F) of NL530.

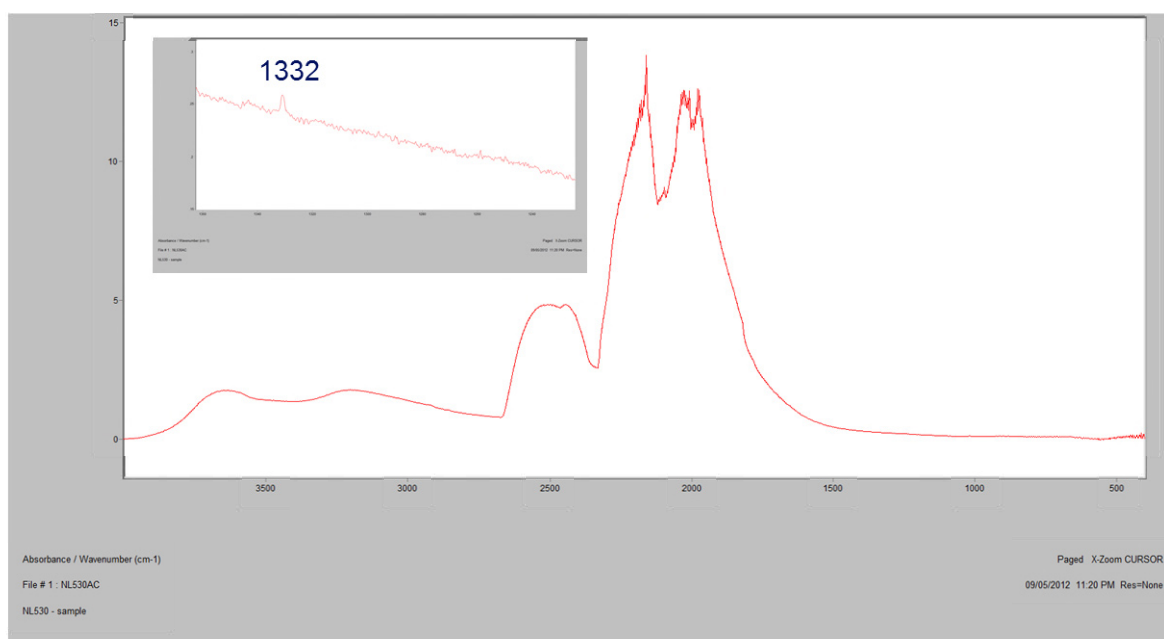


Figure 7: FTIR spectra of NL530. The inset shows a close-up of the one-phonon region of the spectrum.

No 3123 cm^{-1} feature (corresponding to the defect NVH^0) was detected in this sample. The absence of this feature is consistent with post-growth annealing, as although the 3123 cm^{-1} line is commonly observed in as-grown nitrogen-containing CVD synthetics, it is removed by annealing at 1800°C .

3.6 Photoluminescence spectroscopy

Photoluminescence data were recorded using the Horiba Labram HR system with the sample held at 77K using a continuous flow Oxford Instruments MicroStat. We compared the PL spectra of sample NL530 with a Gemesis CVD synthetic diamond (NL486-02) that we have previously investigated. The PL spectra are shown in Figure 8. The spectra were very similar to other Gemesis CVD synthetic

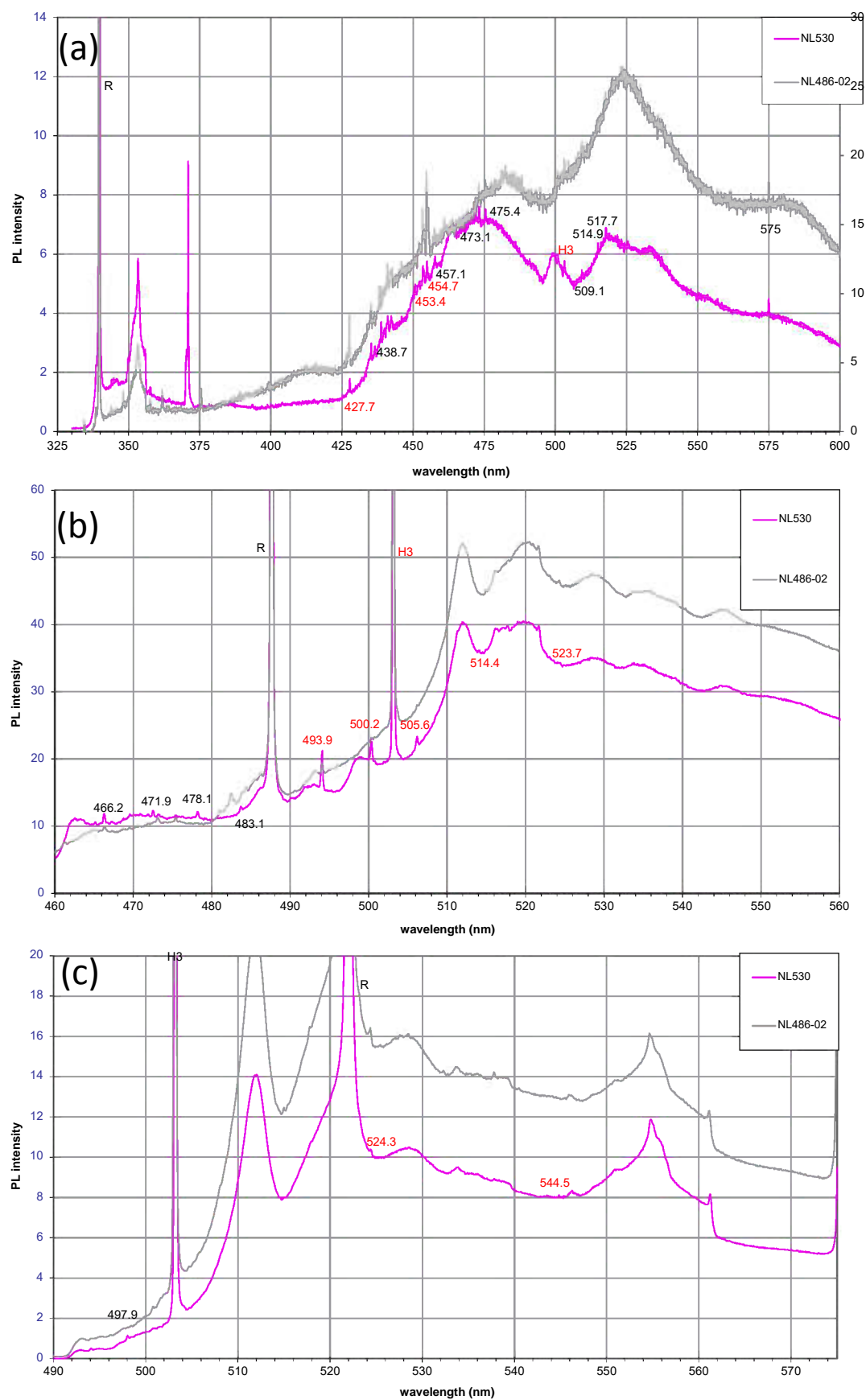
diamond samples that we have measured in the past, and the features showed a good correlation with those present in samples generated in De Beers research that have been annealed in the range of 1900-2000°C. In each Figure, the wavelengths of the PL features that suggest high-temperature treatment are marked out in red.

The following points are worthy of mention:

- The spectra for NL530 are similar to those for NL486-02; also note that the Raman normalised intensities measured 503 nm (H3, nitrogen – vacancy – nitrogen complex in the neutral charge state), 575 nm (nitrogen-vacancy defect in the neutral charge state), 637 nm (nitrogen-vacancy defect in the negative charge state) and 737 nm (silicon-vacancy defect in the negative charge state) zero phonon lines (shown in Table 4) for the two samples are very similar. This suggests a reproducible overall production process.
- In 325 nm excitation, a broad luminescence band is observed which peaks around 525 nm.
- 458 and 488 nm excitations show only moderate H3 luminescence, which is not surprising as the nitrogen concentration is low. The 575 and 637 nm lines are fairly weak. (Their Raman normalised intensities with 514 nm excitation were found to be only 0.04.) Although the nitrogen defects responsible for these lines are grown into plasma enhanced CVD synthetic diamond when nitrogen is present in the synthesis environment, their intensity tend to be reduced by heat treatment. $I_{503} / (I_{575} + I_{637}) = 1.3$ and this is close to the value (~ 1.5) recorded for NL486-02 and also consistent with values measured for samples in the De Beers research programme that were annealed between 1800 and 1900°C. Note that the observation of H3 for a sample with such a low nitrogen content is a strong indicator that the sample has been annealed as it would not be present in as-grown CVD synthetics containing such a low concentrations of nitrogen.
- Several weak lines between 520 and 570 nm confirm that the samples have been annealed. The spectra in this region are most similar to De Beers Technologies UK spectra of samples that were annealed at 1900 and 2000°C.
- The 737 nm line is not particularly strong in NL530; it is only a fraction of the Raman intensity but is slightly stronger than was measured for NL486-02.

Sample	503/R	575/R	637/R	637/575	737/R
NL530	0.104	0.04	0.04	1	0.021
NL486-02	0.122	0.04	0.04	1	0.017

Table 4: Raman normalised photoluminescence intensity data for the 503, 575, 637 and 737 nm zero phonon lines for the Gemesis sample NL530



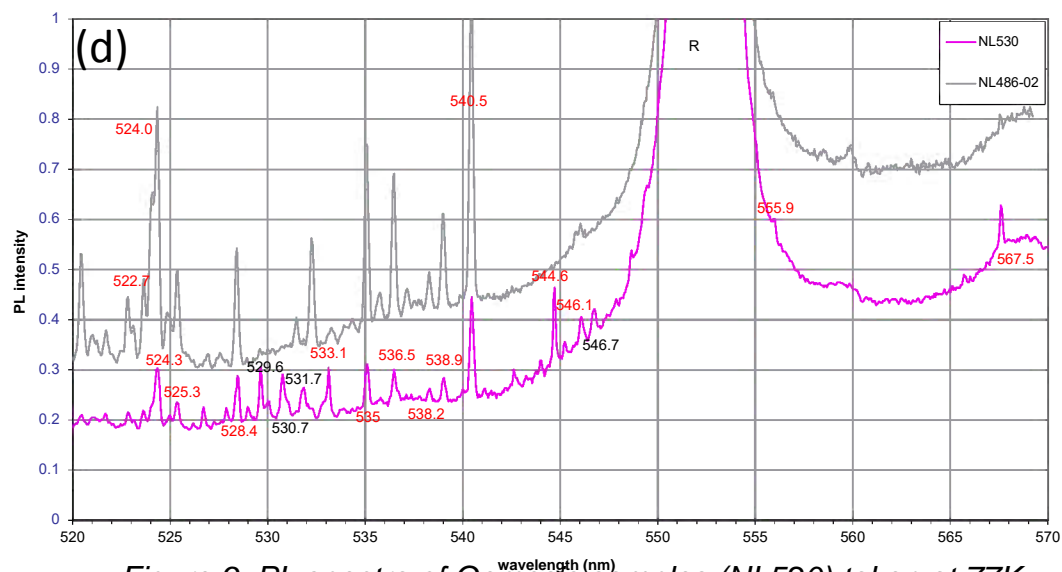
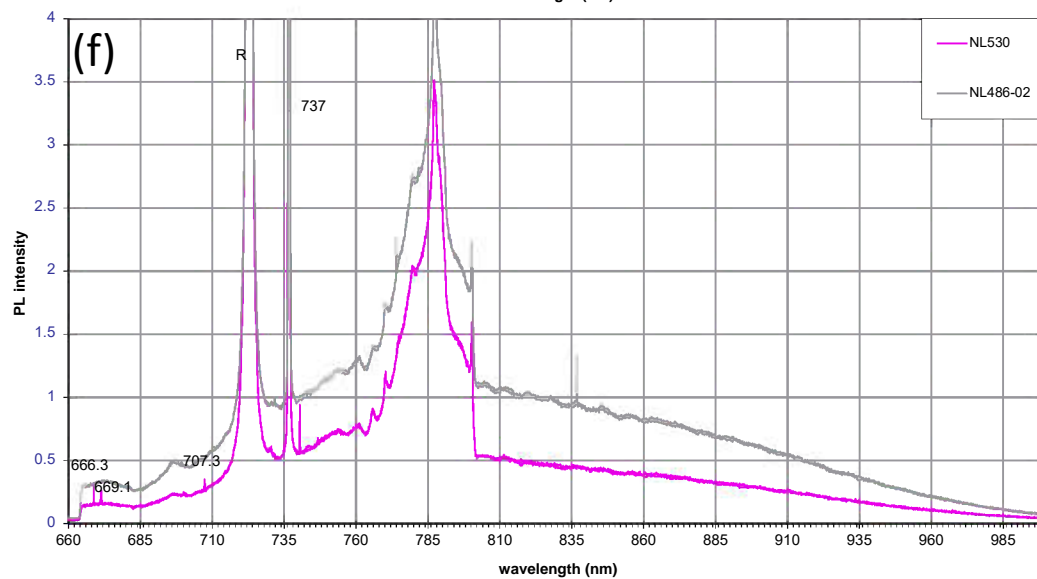
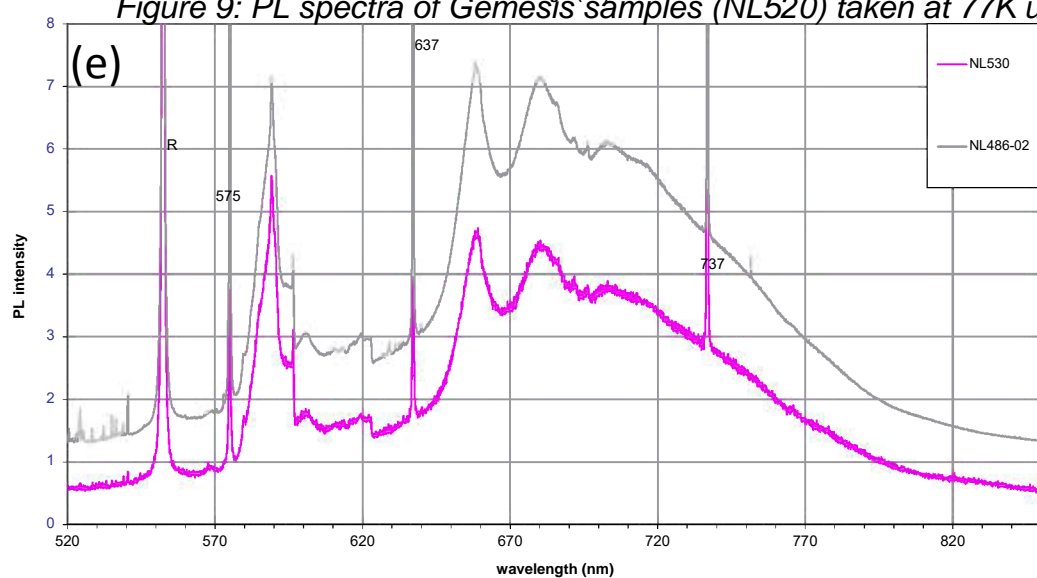


Figure 9: PL spectra of Gemesis samples (NL520) taken at 77K u



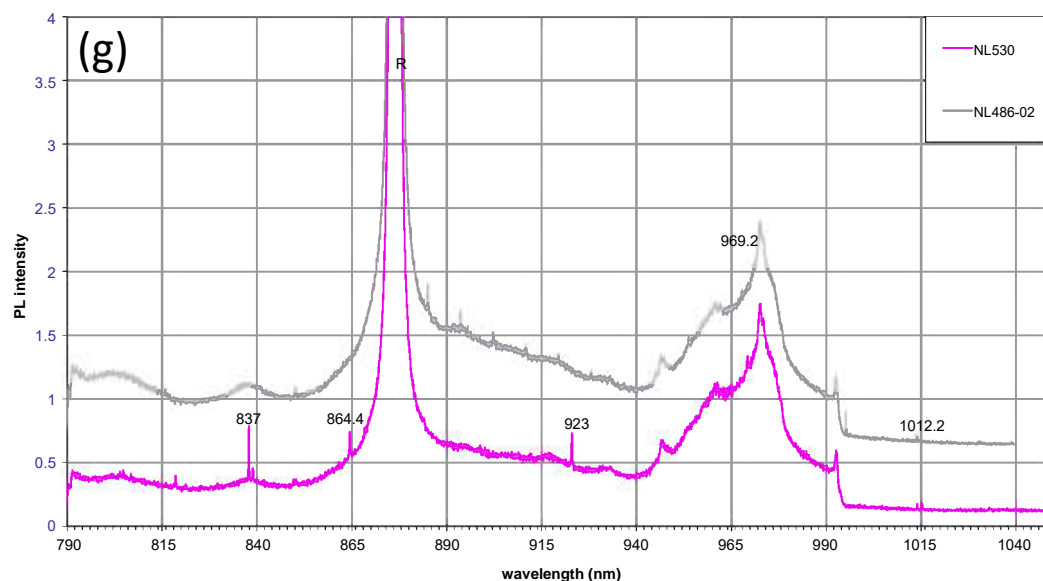


Figure 8: Photoluminescence spectra of sample (NL530) recorded at 77K with (a) 325 nm, (b) 458 nm, (c) 488 nm, (d) 514 nm (520-570 nm range), (e) 514 nm, and (f) 660 nm (g) 785 nm excitation. Data from another Gemesis sample (NL486-02) are also shown for qualitative comparison only.

3.7 Processing of sample prior to optical analysis

Gemstone NL530 was processed into a parallel-sided plate for optical analysis. Images of the final processed sample are shown in Figure 9. The culet was first removed by laser sawing. Then the exposed facet was polished (after the first polish, a UV-visible spectroscopy measurement was taken). Then, both the new facet and the table were polished to enlarge the parallel-sided region of the sample available for birefringence analysis. The girdle (containing the inscription) remained largely intact throughout the processing steps but the inscribed word “GEMESIS” appears to have been partially erased, possibly as a result of the way the stone was held during polishing. After processing, the plate produced from NL530 weighed 0.20 ct and had a thickness of 0.72 mm (z) and a diameter of 4.74 mm.



Figure 9: Images of NL530 (including girdle inscription) after it had been processed into a parallel sided plate. An image of the girdle inscription before processing is shown for comparison (see also figure 4).

3.8 UV-visible spectroscopy

A room temperature UV-visible spectrum of the parallel-sided plate produced from NL530 was recorded using a Perkin-Elmer Lambda 1050 spectrophotometer (see Figure 10). The sample was not exposed to UV radiation prior to measurement.

By minimising the strength of N_S^0 absorption by subtracting with a calibrated spectrum of type Ib diamond, a $[N_S^0]$ value of 0.17 ppm was deduced. This low value is consistent with the non-observation of the 1344 cm^{-1} peak in the FTIR spectrum. Comparison of the shape of the spectrum with that for N_S^0 indicates that there is a slight residual absorption that does not derive from N_S^0 . The shape of this residual suggests that the high-temperature treatment had not been entirely effective at removing absorption responsible for brown colour.

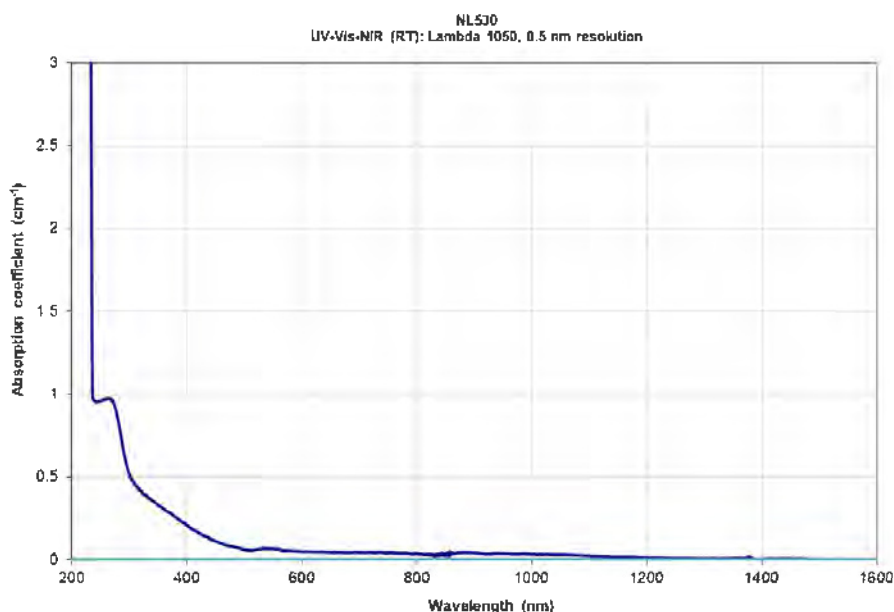


Figure 10: Room-temperature UV-visible absorption spectrum of NL530. The best fit to the 270 nm absorption feature indicated a $[N_S^0]$ value of 0.17 ppm.

3.9 Electron paramagnetic resonance (EPR)

EPR measurements were performed on the round brilliant NL530 (weight: 0.40 ct). They were performed at Warwick University and were received on 18 Sept 2012. Two measurements were taken in rapid-passage mode: one after the sample had been illuminated with above bandgap UV radiation and the other after heating of the sample in the dark to 500°C .

$[N_S^0]$ values were determined by comparison with a standard diamond reference with a known concentration of N_S^0 . These N_S^0 values measured for NL530 are shown in Table 5. We note a good agreement between the values deduced using EPR measurements on the round brilliant and that deduced using UV-visible absorption spectroscopy measurements on the polished plate produced from the round brilliant. A slight reduction in measured $[N_S^0]$ after heating of the sample in the dark is consistent with thermal excitation of electrons to the conduction band

and trapping at other defects present in the sample. De Beers research has indicated that this process is reversed by illumination with above band gap UV radiation.

	Weight (ct)	$[N_s^0]$ (ppm)	$[N_s^0]$ (cm^{-3})
After UV illumination	0.40	0.160 ± 0.02	$2.8 \pm 0.3 \times 10^{16}$
After heating	0.40	0.130 ± 0.02	$2.3 \pm 0.3 \times 10^{16}$

Table 5: N_s^0 concentration values deduced using EPR spectroscopy for the round brilliant NL530. Measurements were recorded after UV illumination and also after heating in the dark to 500°C.

3.10 Measurement of absorption coefficient at 1.06 μm

The parallel-side plate produced from NL530 was sent to Laser Zentrum Hannover for laser calorimetry measurements of absorbance at 1064 nm (1.064 μm). The measurement was carried out on 23 January 2015. The method used and the results are given in the LZH report number 14650. The method followed ISO 11551 and gave an absorbance result for the NL530 plate of 1727 ppm (1727×10^{-6}). From this result and the thickness of the plate an absorption coefficient at 1064 nm of $0.024(3) \text{ cm}^{-1}$ was deduced.

3.11 Metripol analysis of optical quality

The parallel-sided plate was analysed using the Metripol microscope at Warwick University using an illumination wavelength (λ_{meas}) of 590 nm to give $\sin \delta$ values pixel-by-pixel. A series of overlapping images was collected using a 4x objective, which provides a 1360 x 1024 pixel image covering 1.581 x 1.191 mm area with an approximate pixel size of 1.163 x 1.163 μm . The overlapping images were then stitched together to create one image of the entire area of the sample. The image stitching was completed using the free program “ImageJ” with the “stitching” plugin. This program allows the user to manually place individual image frames into position. The frame positions can then be computationally optimised and a stitched image / mosaic is generated along with a text file containing the optimized frame positions. De Beers Technologies UK have used a Matlab script, to stitch .ssf (data) files into an image using the optimized frame positions. A Matlab script has also been used to select and analyse appropriate square or rectangular regions of interest from the .ssf data image, (Figures 11 and 12). A complete description of the analysis and experimental technique is available in an internal report “Mapping samples using the Metripol and analysis using imageJ and Matlab”.

Two square regions of the sample image were selected as illustrated in Figure 11. These areas had dimensions of 1.3 mm x 1.3 mm and 2.5 mm x 2.5 mm. Histograms of $\sin \delta$ for selected areas can be created as illustrated in Figure 12.

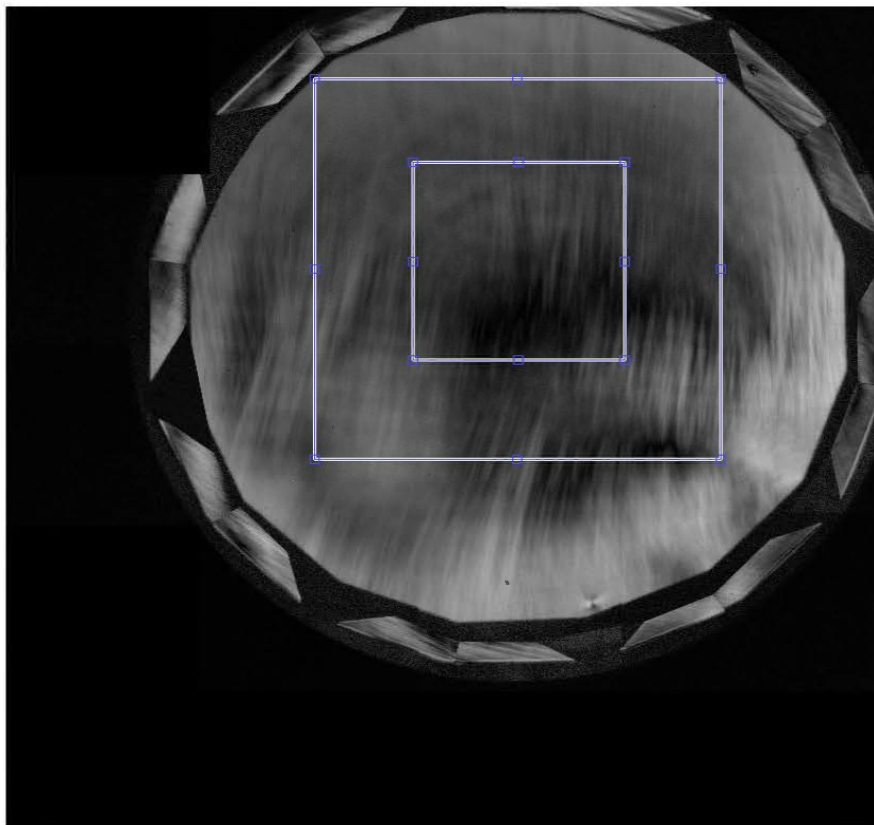


Figure 11: Square regions of the sample selected for analysis of the distribution of $\sin \delta$ values. The dimensions of these regions were 1.3 mm x 1.3 mm and 2.5 mm x 2.5 mm.

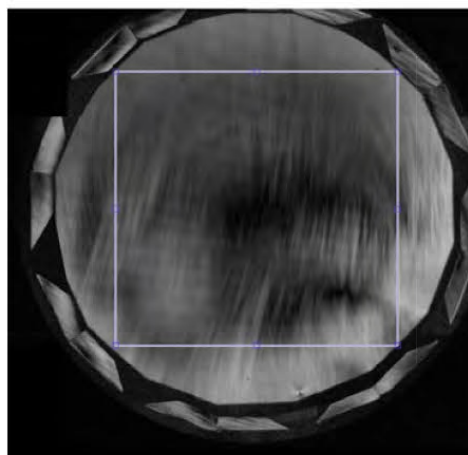
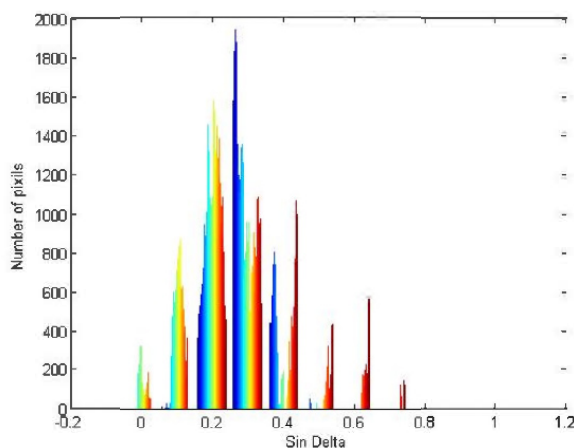


Figure 12: A histogram of values of $\sin \delta$ values for the 2.73 x 2.89 mm region, with a position shown by the white box in the image on the right.

For the two selected areas (shown in figure 11) the maximum $\sin \delta$ value was found ($\sin \delta_{\max}$), and hence δ_{\max} was calculated.

Using the equation $\Delta n_{\max} = \delta_{\max} \lambda_{\text{meas}} / 2\pi L$, Δn_{\max} was then deduced. The results are given in Table 6. For the selected 1.3 mm x 1.3 mm area the birefringence remains in first order (ie δ is less than $\pi/2$ radians) and $\sin \delta$ and $|\sin \delta|$ do not

exceed 0.352(20). Over the 2.5 mm x 2.5 mm area the birefringence remains in first order and $\sin \delta$ and $|\sin \delta|$ do not exceed 0.573(20). This table also includes $\sin \delta_{\max}$ and Δn_{\max} values after selection of the pixels with the 99% and 98% lowest values. Consideration of possible sources of measurement error indicates that the measured $\sin \delta_{\max}$ values are within 0.02 of the true values and the Δn_{\max} values are within 3×10^{-6} of the true values.

Dimension of selected area (mm)	$\sin \delta_{\max}$ (for 100% of the analysed area)	Δn_{\max} (for 100% of the analysed area)	$\sin \delta_{\max}$ (for 99% of the analysed area)	Δn_{\max} (for 99% of the analysed area)	$\sin \delta_{\max}$ (for 98% of the analysed area)	Δn_{\max} (for 98% of the analysed area)
1.3 x 1.3	0.352	4.69×10^{-5}	0.302	4.0×10^{-5}	0.291	3.85×10^{-5}
2.5 x 2.5	0.573	7.96×10^{-5}	0.427	5.75×10^{-5}	0.412	5.54×10^{-5}

Table 6: $\sin \delta_{\max}$ and Δn_{\max} values for selected regions over the NL530 plate. Values are given for 100% of the analysed area and for 99% and 98% of the analysed area.

4. CONCLUSION

This Gemesis round brilliant is very similar to many Gemesis CVD synthetics that De Beers Technologies UK have studied. The F colour grade means that it can be described as colourless, a descriptor generally reserved for stones with colour grades of D, E or F. It is clear from DiamondView images and PL spectroscopy that the sample is CVD synthetic in origin. The PL spectroscopy results the DiamondView images indicate that it has been annealed after growth, most likely in the range of 1900-2000°C. Using the instruments developed by De Beers Technologies UK and sold by IIDGR, gemmological laboratories should find such synthetic diamonds relatively easy to identify. The DiamondView images, in particular, should be straightforward to interpret.

We have noted similar nitrogen concentrations in different Gemesis diamond samples that we have investigated and this is unlikely to have resulted if the presence of nitrogen is accidental. It is therefore likely that the CVD synthesis employed involves intentional addition of nitrogen to the growth environment.

The plate produced from NL530 was found to have an absorption coefficient of $0.024(3) \text{ cm}^{-1}$ at a wavelength of $1.06 \text{ }\mu\text{m}$. The plate showed only first order birefringence. Over a selected 1.3 mm x 1.3 mm area $\sin \delta$ and $|\sin \delta|$ do not exceed 0.352(20), and over a selected 2.5 mm x 2.5 mm area $\sin \delta$ and $|\sin \delta|$ do not exceed 0.573(20). Over the 1.3 mm x 1.3 mm area the maximum Δn value was $4.69(30) \times 10^{-5}$ and for the 2.5 mm x 2.5 mm area the maximum Δn was $7.96(30) \times 10^{-5}$.

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TECHNICAL REPORT

Title: Summary of Evidence that NL530 had been Heat Treated (Annealed) after Growth

Authors: Philip Martineau

Date: 5 October 2016

1. Introduction

NL530, a 0.40 ct CVD synthetic diamond round brilliant bought from Gemesis, was delivered to De Beers Technologies UK on 8 May 2012. It was characterized before being processed to produce a parallel-side plate for birefringence investigation. This short report presents some key findings of the initial characterization that provide evidence that the material had been annealed after growth.

2. Absorption spectroscopy

UV/visible absorption spectrum of NL530 recorded at room temperature only showed the 270 nm absorption feature associated with single substitutional nitrogen. The strength of the feature indicates that the approximate concentration of single substitutional nitrogen is 0.17 ppm.

The EPR spectrum indicated that the concentration of neutral single substitutional nitrogen was approximately 0.13 ppm after heating in the dark and 0.16 ppm after exposure to UV radiation.

The FTIR absorption spectrum shows very little extrinsic absorption but there is a small absorption peak at 1332 cm^{-1} consistent with a low concentration (upper concentration limit: 0.11 ppm) of positively charged single substitutional nitrogen.

3. Photoluminescence spectroscopy

Photoluminescence spectra from NL530 were recorded at liquid nitrogen temperature for various excitation wavelengths and some of the key photoluminescence lines observed are listed in table 1.

Excitation wavelength (nm)	PL features shown by NL530	Notes
325	427.7, 453.4, 454.7, H3	Lines not seen in as-grown material
458	Strong H3	$I(\text{H3})/I(\text{Raman}) = 0.104$
488	H3: 503 nm	Strong H3 consistent with heat treatment
514	544.6 nm, NV^0 : 575 nm, NV^- : 637 nm	$I(\text{NV}^0)\text{ ZPL and }I(\text{NV}^-)\text{ ZPL} \approx 0.04 \times \text{Raman}$, Observation of 544.6 nm PL suggests annealing
660	737 nm	$I(737)/I(\text{Raman}) = 0.021$

Table 1 Key zero phonon lines (ZPL) present in photoluminescence spectra of NL530 recorded at liquid nitrogen temperature with various different laser excitation wavelengths

Table 2 lists Raman normalized intensities for some zero phonon lines present in photoluminescence spectra of NL530, along with other intensity ratios derived from the measurements.

$I(\text{NV}^0 \text{ ZPL})/I(\text{Raman})$	0.04
$I(\text{NV}^- \text{ ZPL})/I(\text{Raman})$	0.04
$I(\text{NV}^- \text{ ZPL})/I(\text{NV}^0 \text{ ZPL})$	1
$I(\text{H3 ZPL})/I(\text{Raman})$	0.104
$I(\text{H3 ZPL})/I(\text{NV}_{\text{total}})$ where $I(\text{NV}_{\text{total}}) = I(\text{NV}^0 \text{ ZPL}) + I(\text{NV}^- \text{ ZPL})$	1.3

Table 2 Raman normalized zero phonon line (ZPL) intensities for various defect centres

Previous investigations of the effect of heat treatment on the properties of CVD synthetic diamond samples produced by Element Six for research purposes have indicated that the ratio of the intensity of the H3 zero phonon line to the summed intensities of the NV^0 and NV^- zero phonon lines is changed by post-growth heat treatment (sometimes called annealing) in the way shown in figure 1. It can be seen from this figure that there is a marked increase of the ratio as a function of annealing temperature and measurements on a range of different samples have indicated that the ratio can be used as a reliable indicator of whether or not a sample has been post-growth heat treated and the approximate temperature of such heat treatment. The value of the ratio measured for NL530 is shown in figure 1 and indicates a heat treatment temperature of between 1900 and 2300°C.

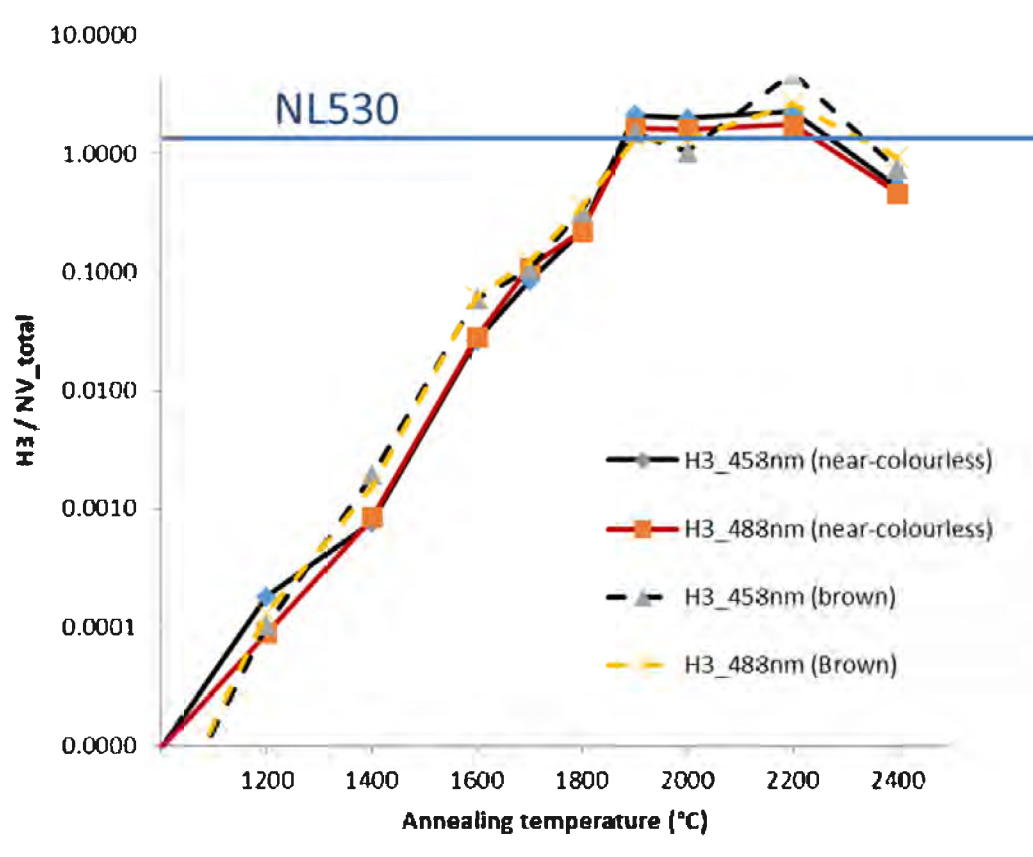


Figure 1 The ratio of H3/NV fluorescence intensities as a function of annealing temperature for brown and near-colourless CVD synthetic diamond. Results are shown for two different excitation wavelengths: 458 nm and 488 nm. The ratio for NL530 is shown by the horizontal line and suggests a heat treatment temperature in the approximate range 1900-2300°C.

4. DiamondView images

In the DiamondView instrument, samples are illuminated with above bandgap radiation and images are then captured of the resulting surface fluorescence and phosphorescence. The instrument is used by the diamond trade (eg grading laboratories) for identification of natural and synthetic diamond. It is also a useful sample characterization tool for research into the effects of heat treatment of synthetic diamond and in the course of such research carried out at De Beers Technologies we have captured images of CVD synthetic diamond samples of various kinds in their as-grown form and after heat treatments at different temperatures. **Figure 2** shows a series of DiamondView images of CVD synthetic diamond samples annealed at successively higher temperatures.

	<i>Microscopy Initial</i>	<i>DiamondView Initial</i>	<i>Microscopy T1</i>	<i>DiamondView T1</i>	<i>DiamondView (phosph.) T1</i>
1200°C / 4h DTC					none
1400°C / 4h DTC					none
1600°C / 4h 1aM					none
1700°C / 4h 1aM					
1800°C / 4h 1aM					
1900°C / 4h 1aM					
2000°C / 4h 1aM					
2200°C / 4h 1aM					
2400°C / 4h 1aM					

Figure 2 Microscopy and DiamondView images of CVD synthetic diamond samples heat treated at different temperatures. (The 1200 and 1400°C heat treatments were carried out at atmospheric pressure but for the other heat treatments diamond stabilizing pressure was applied.)

It can be seen from figure 2 that as the temperature of the heat treatment applied to brown CVD synthetic diamond is increased

- i) the brown colour is removed,
- ii) the dominant fluorescence colour changes from orange to green and then to blue

iii) green phosphorescence appears and then, at higher temperatures, the dominant colour of the phosphorescence changes from green to blue.

DiamondView images of NL530 are shown below in figure 3 (fluorescence) and figure 4 (phosphorescence). The dominant colour of the fluorescence and together with the observation of blue phosphorescence is not consistent with what is observed for as-grown nitrogen-doped CVD diamond but is consistent with what would be expected for nitrogen-doped CVD synthetic diamond material that has been heat treated at high temperatures as illustrated in figure 1. Matching of the fluorescence/phosphorescence colours suggests a heat treatment temperature in the approximate range 2000-2200°C in agreement with the range indicated by the photoluminescence intensity ratio method outlined in section 3.

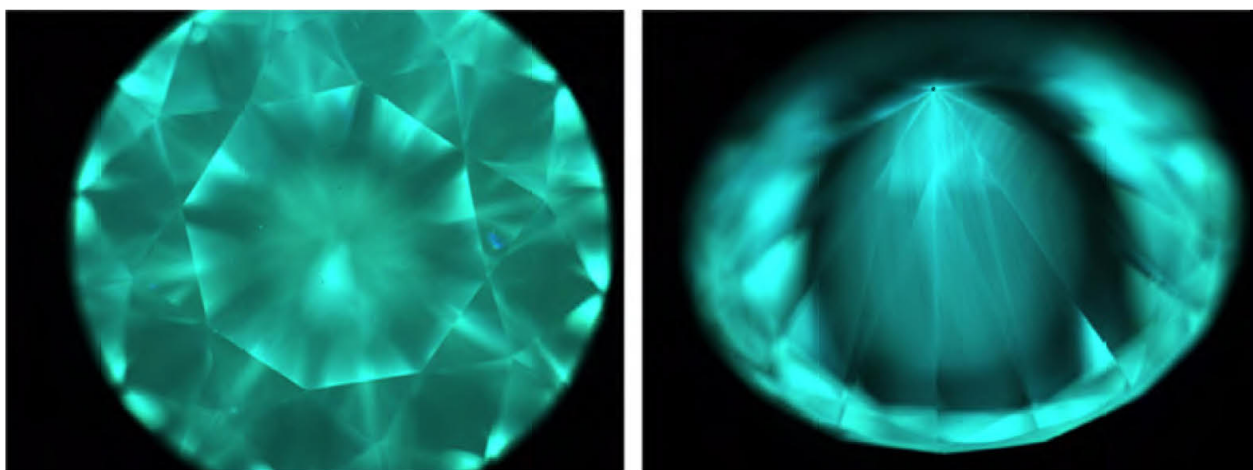


Figure 3 DiamondView fluorescence images of NL530

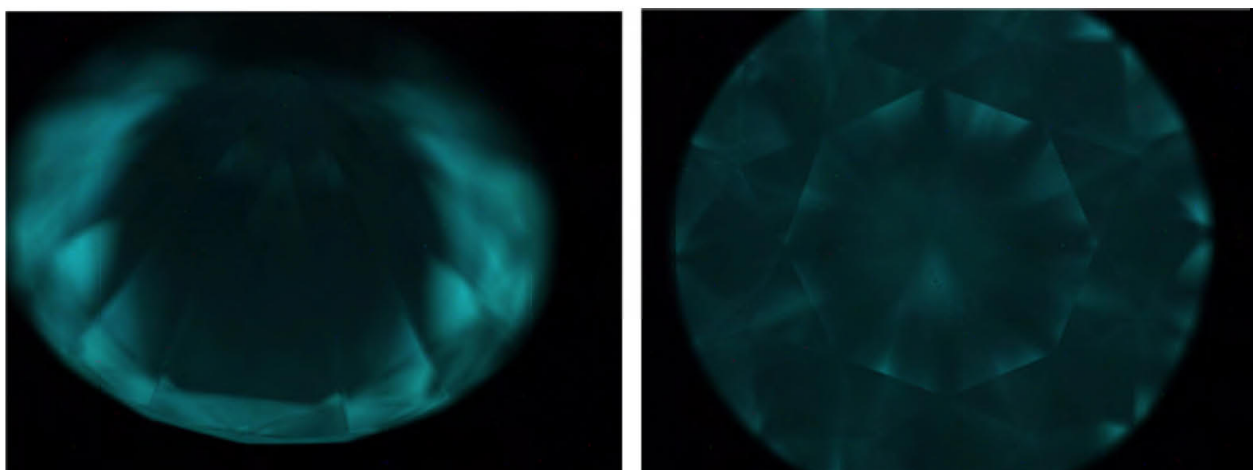


Figure 4 DiamondView phosphorescence images of NL530

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452**5. Summary of characteristics of optical grade CVD synthetic diamond plates sold by Microwave Enterprises and changes observed after heat treatment**

As detailed in this short report, characterization of the CVD synthetic diamond sample NL530 bought from Gemesis has strongly indicated that it has been heat treated after growth. We have, however, also had the opportunity to study ten CVD synthetic diamond plates (NL625-1 to -10) sold by Microwave Enterprises for optical applications and stated by them to have been produced by Ila Technologies and we found these samples to have characteristics consistent with their not having been heat treated after growth. This gave us the opportunity to investigate the effect of heat treatment on material grown by Ila Technologies. NL625-01 was heat treated at 2100°C for 30 minutes and NL625-06 was heat treated at 2400°C for 30 minutes. The effect on the fluorescence and phosphorescence characteristics is illustrated in figure 5.

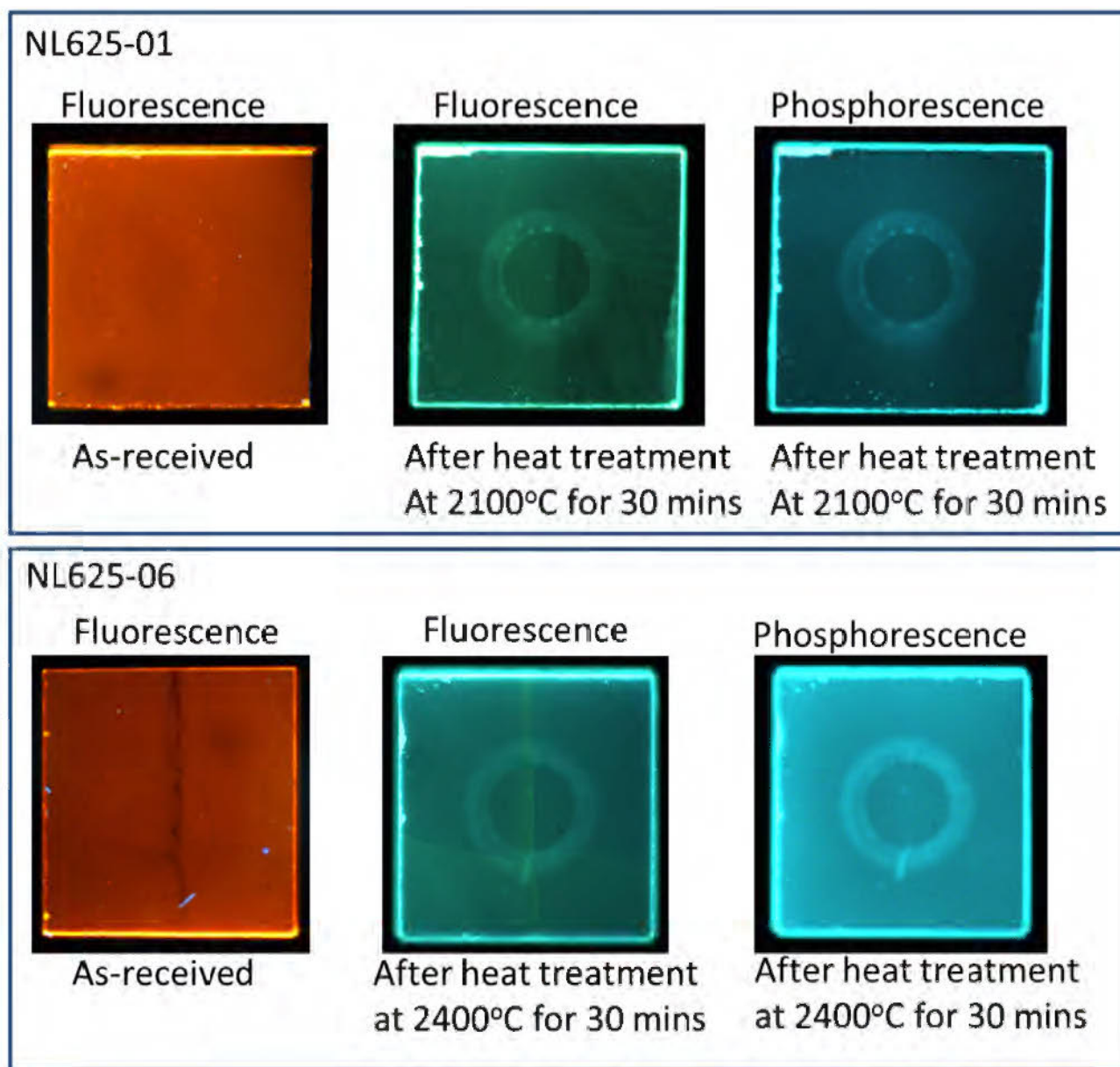


Figure 5 DiamondView images of NL625-01 and NL625-06 before and after heat treatment. Neither sample showed phosphorescence in their as-received form.

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Photoluminescence spectra of all ten of the samples NL625-01 to -10 in their as-received form showed strong 575 and 637 nm lines from NV defects (with 514 nm excitation) and no H3 luminescence (with either 488 nm or 458 nm excitation). Although they were stated to be for optical applications they were brown and their UV/visible absorption spectra showed the gradual rise in absorption towards shorter wavelengths that is typical of as-grown nitrogen-doped CVD synthetic diamond samples. EPR spectroscopy indicated that they contained between 0.063 and 0.225 ppm of single substitutional nitrogen (NL625-01: 0.225 ppm and NL625-06: 0.100 ppm).

Detailed photoluminescence spectroscopy of the heat treated samples has not been carried out but comparison of figures 2 and 5 shows that the heat treated samples have DiamondView fluorescence and phosphorescence characteristics very similar to those of samples that we had previously grown and heat treated in the same temperature range as part of our experimental programme.

Comparison of figure 5 with figures 3 and 4 shows that the DiamondView fluorescence and phosphorescence characteristics of NL530 are very similar to those of the two NL625 samples that we heat treated at high temperatures.

6. Discussion

CVD diamond grown with nitrogen present in the growth environment tends to be brown and to contain nitrogen in forms such as single substitutional nitrogen, nitrogen-vacancy (NV) centres and nitrogen vacancy hydrogen (NVH) centres. Single substitutional nitrogen gives rise to the absorption feature at 270 nm and the P1 lines in the EPR spectrum. NV defects give rise to 575 and 637 nm luminescence features observed when a sample is excited at 514 nm, for example. NVH defects are responsible for the 3123 cm^{-1} line in the FTIR spectrum and a band at about 520 nm in the visible absorption spectrum.

When such CVD diamond is heat treated at high temperatures NVH defects are dissociated and as a result the 3123 cm^{-1} line and the 520 nm band are no longer observed. NV centres dissociate but low concentrations of these defects remain because of a dynamic equilibrium between their formation and loss. As a result the NV fluorescence intensity is reduced but weaker NV luminescence is still observable for nitrogen containing heat treated CVD diamond. Single substitutional nitrogen remains after heat treatment and in addition some nitrogen is found in an aggregated form known as the H3 centre. This is made up of two nitrogen atoms with a neighbouring missing carbon atom (vacancy). Our research has shown that as nitrogen containing CVD diamond is heat treated at successively higher temperatures, for given excitation conditions the ratio of the H3 luminescence intensity to the NV luminescence intensity increases in a way that enables the approximate temperature of heat treatment to be deduced from measurement of this ratio. For as-grown samples the H3 fluorescence is generally absent and NV fluorescence is strong.

The effect of heat treatment on defect centres responsible for fluorescence (NV centres and H3) also helps to explain the changes in the colours of the fluorescence observed in DiamondView images when samples are heat treated. Heat treatment reduces the concentration of NV centres that show orange/red fluorescence and increases the intensity of H3 centres that show green fluorescence. Additional blue fluorescence is introduced when samples are annealed at the highest temperatures.

For NL530 the results of absorption spectroscopy are consistent with heat treatment because of the absence of absorption from defects that are typically grown into CVD diamond but would be

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removed by heat treatment. The results of photoluminescence spectroscopy and DiamondView imaging provide strong evidence that NL530 has been heat treated and indicate a heat treatment in the approximate range 1900-2300°C.

Samples received from Microwave Enterprises had characteristics consistent with their being in their as-grown form (not having been heat treated to high temperatures after growth). When two of these samples were heat treated at 2100°C and 2400°C, after the heat treatment their DiamondView characteristics were very similar to those of NL530. This indicates that when material grown by Ila Technologies is heat treated at high temperatures its DiamondView characteristics change dramatically from orange fluorescence and no phosphorescence (in the as-grown form) to blue/green fluorescence and blue phosphorescence (after heat treatment). NL530 showed blue/green fluorescence and blue phosphorescence and this is therefore additional evidence that it had been heat treated at high temperatures.

Philip Martineau

Senior Manager Physics at De Beers Technologies UK

September 2016

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TECHNICAL REPORT

Title: Analysis of Pure Grown Diamonds Gemstone NL702
Authors: Philip Martineau and Brad Cann
Date: 5 October 2016

1. SUMMARY

A synthetic round brilliant (NL702) with a weight of 0.38 ct, was examined at De Beers Technologies UK. It had been sold to Ayako Lawson by Pure Grown Diamonds and it was received with an IGI grading report (report number LG10226420) that indicated that IGI had given it K colour and VS1 clarity grades. The girdle of the stone was laser inscribed "LAB GROWN LG10226420". The characteristics of this synthetic diamond round brilliant were very similar to those of Gemesis CVD synthetics we have examined in the past. DiamondSure referred the synthetic diamond as type IIa, and DiamondPLus has referred it as a CVD synthetic diamond due to the presence of the 737 nm photoluminescence line. DiamondView images showed striations providing evidence that the round brilliant was CVD synthetic in origin. FTIR spectroscopy indicated a concentration of single substitutional nitrogen of 0.5 ppm. A plate (with a thickness of 0.71 mm, a diameter of 4.56 mm and a weight of 0.18 ct) was processed from the stone. After processing and cleaning, the girdle inscription was only partially visible, suggesting that it had been extremely shallow and had originally been visible principally because of surface graphitisation which had been removed in cleaning. EPR spectroscopy at Warwick University has shown that the parallel-sided plate of CVD synthetic diamond contained neutral single substitutional nitrogen at a concentration of 460(40) ppb ($8.1 \times 10^{16} \text{ cm}^{-3}$). Measurements carried out by Laser Zentrum Hanover indicated that the absorption coefficient of the plate at $1.06 \mu\text{m}$ was $0.044(5) \text{ cm}^{-1}$. Optical analysis was performed on the plate at Warwick University using a Metripol microscope. The results indicated that the plate produced from NL702 possesses good optical quality. Only first order birefringence was observed. Over a $1.3 \text{ mm} \times 1.3 \text{ mm}$ selected area $\sin \delta$ and $|\sin \delta|$ do not exceed 0.141(20). Over a selected $2.5 \text{ mm} \times 2.5 \text{ mm}$ area $\sin \delta$ and $|\sin \delta|$ do not exceed 0.447(20). For the $1.3 \text{ mm} \times 1.3 \text{ mm}$ area the maximum Δn value was $1.87(30) \times 10^{-5}$ and for the $2.5 \text{ mm} \times 2.5 \text{ mm}$ area the maximum Δn was $6.13(30) \times 10^{-5}$.

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2. INTRODUCTION

A round brilliant polished gemstone of 0.38 ct weight was received from Ayako Lawson at De Beers Technologies UK on 2 November 2015. It was assigned sample number NL702. Along with the sample, documentation indicating its origin was supplied. This included an invoice and packing note from Pure Grown Diamonds (please see Figures 1 & 2). Both were dated 27 October 2015. An IGI certificate (Figure 3) was also supplied with the sample. The sample carried a laser inscription on its girdle: "Lab Grown LG10226420. Details of the sample are listed in Table 1.



PURE GROWN DIAMONDS INC.
 28 WEST 44TH STREET,
 SUITE 1204,
 N.Y.C. NEW YORK
 USA
 Phone No: 646-652-8927
 Fax No: 646-800-3449
 EMail:
 Web Site: <http://www.puregrowndiamonds.com/>

Invoice

Invoice No: SA-1510-00178
 DATE: 27/Oct/2015
 Remarks:
 Payment Terms: 0
 Packing List No:

Buyer MRS. AYAKO LAWSON 2 ASTOR CLOSE MAIDENHEAD, S161XQ U.K. Tel : 441628298790 Fax : EMail :		Consignee MRS. AYAKO LAWSON 2 ASTOR CLOSE MAIDENHEAD, S161XQ U.K. Tel : 441628298790 Fax : EMail :			
SNo	Description	Qty	CTS	RATE US \$ / CTS	AMOUNT US \$
1	LAB GROWN CUT & POLISHED DIAMONDS	2	0.380	1,958.44	1,045.09
	DISCOUNT AMT				(0.00)
	SHIPPING AMT				100.00
	OTHER CHARGES AMT				0.00
	TAX AMT				0.00
	TOTAL	2	0.380		1,745.09
Amount in Words - US DOLLAR - ONE THOUSAND SEVEN HUNDRED FORTY-FIVE AND NINE CENTS ONLY					
1. The above mentioned items are LAB GROWN DIAMONDS and/or jewelry that contains of Lab Grown Diamonds. These diamonds are grown by man. 2. The origin of these diamonds, as well as the process to grow these diamonds, are in a fully conflict free and ecologically friendly environment. 3. They are optically, chemically and physically identical to mined diamonds. 4. All subsequent future sales of these diamonds must be accompanied by appropriate disclosure as to their origin.		FOR PURE GROWN DIAMONDS INC.		FOR MRS. AYAKO LAWSON	

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Figure 1: Scanned copy of the invoice received with NL702

 PURE GROWN DIAMONDS <small>CERTIFIED & SUSTAINABLE</small>	PURE GROWN DIAMONDS INC. 28 WEST 44TH STREET, SUITE 120A, NYC, NEW YORK USA Phone No: 646-652-8927 Fax No: 646-808-3449 Email: Web Site: http://www.puregrowndiamonds.com/	DATE: 27/01/2015 Packing List No:
	SHIP TO: MRS. AYAKO LAWSON 2 ASTOR CLOSE MAIDENHEAD, SL6 1XQ U.K. Tel: 441628298790 Fax: Email:	SHIP TO: MRS. AYAKO LAWSON 2 ASTOR CLOSE MAIDENHEAD, SL6 1XQ U.K. Tel: 441628298790 Fax: Email:

PACKING LIST OF LABORATORY GROWN DIAMONDS


QTY	DETAILS	SHAPE	SIZE	COLOR	CLARITY	PCS	CTS	RATE	VALUE
1	LG10226420	ROUND	0.30-0.39	K	VS1	1	0.300	1,375.50	522.69
2	LG10172714	PRINCESS	0.40-0.49	K	VS1	1	0.400	2,600.00	1,122.00
						2	0.800		1,645.89
<div> <p>1. The above mentioned items are LAB GROWN DIAMONDS and/or jewelry that contains of Lab Grown Diamonds. These diamonds are grown by man.</p> <p>2. The origin of these diamonds, as well as the process to grow these diamonds, are in a fully conflict free and ecologically friendly environment.</p> <p>3. They are optically, chemically and physically identical to mined diamonds.</p> <p>4. All subsequent future sales of these diamonds must be accompanied by appropriate disclosure as to their origin.</p> </div> <div> <p>FOR:</p> <p>PURE GROWN DIAMONDS INC.</p> </div> <div> <p>FOR:</p> <p>MRS. AYAKO LAWSON</p> </div>									

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Figure 2: Scanned copy of the packing list received with NL702. LG10226420 is the IGI report number for NL702.

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551 Fifth Avenue, New York, NY 10176
Tel: (212) 753-7100 Fax: (212) 758-7759
www.igiworldwide.com

**LABORATORY GROWN
DIAMOND REPORT**

DATE: 6/18/2015 **REPORT NUMBER:** LG10226420

DESCRIPTION: **LABORATORY GROWN DIAMOND**

SHAPE AND CUTTING STYLE: **ROUND BRILLIANT**

MEASUREMENTS: **4.61 - 4.63 x 2.87 MM.**

GRADING RESULT:

Carat Weight: 0.38 CT(S)

Color Grade: K-FAINT COLOR

Clarity Grade: VS1

Cut Grade: IDEAL

PROPORTIONS:

Depth: 62.0%

Table: 57.5%

Crown Height % - Ang ° 15.0% - 35.5°

Pavilion Depth % - Ang ° 43.0% - 40.9°

Girdle: MEDIUM TO SLIGHTLY THICK

Culet: NONE

FINISH:

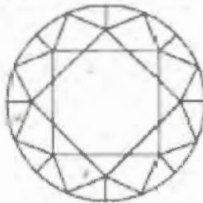
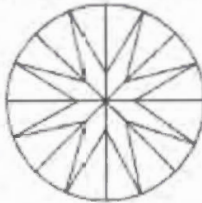
Polish: EXCELLENT

Symmetry: VERY GOOD

FLUORESCENCE: NONE

COMMENTS: Laterscribe ®: "LAB GROWN LG10226420". The laboratory grown diamond described above is classified as Type IIA.

Red symbols denote internal characteristics (inclusions). Green or black symbols denote external characteristics (blemishes). Diagram in an approximate representation of this stone, and symbols shown indicate type, position, and approximate size of clarity characteristics. All clarity characteristics may not be shown. Details of finish are not shown.




PHOTO ENLARGED

COLOR GRADING SCALE	CL		NC		FT		VLT		LT	
	COLORLESS D - F		NEAR COLORLESS G - J		FAINT K - M		VERY LIGHT N - R		LIGHT S - Z	
CLARITY (10X) GRADING SCALE	FL	IF	VVS	VS	SI	I				
	FLAWLESS INTERNALLY FLAWLESS		VERY VERY SLIGHTLY INCLUDED	VERY SLIGHTLY INCLUDED	SLIGHTLY INCLUDED	INCLUDED				

The laboratory grown diamond described in this Report ("Report") has been graded, tested, analyzed, examined and/or inscribed by International Gemological Institute (I.G.I.). A laboratory grown diamond is one that has the same chemical, physical and optical properties as mined diamond, with the exception of being grown by man. I.G.I. employs and utilizes those techniques and equipment currently available to I.G.I., including, without limitation, 10X magnification, corrected triplet loupe and binocular microscope, master color comparison system, non-contact optical measuring device, and such other instruments and/or processes as deemed appropriate by I.G.I. This Report includes advanced security features. The gem and/or article of jewelry will be micro-photographed resulting in an enlarged photograph, as to allow detail to be easily observed. This photograph is representative of the gemstone or jewelry inspected. IT MAY NOT BE YOUR INDIVIDUAL ARTICLE. A duly accredited gemologist or jeweler can advise you with respect to the importance of and interrelationship between cut, color, clarity and carat weight.

THIS REPORT IS NEITHER A GUARANTEE, VALUATION NOR APPRAISAL OF THE LABORATORY GROWN DIAMOND DESCRIBED HEREIN.

© 2007 International Gemological Institute. See Terms and Limitation on Reverse.

Figure 3: A scanned copy of the IGI report for NL702 (report number LG10226420)

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NL702	
Colour grade *,**	K
Clarity grade *,**	VS1
Cut grade **	Ideal
Weight (ct) *,**	0.38
IGI report no. *,**	LG10226420
Grading report date**	18 June 2015

Table 1: Details of the NL702

* indicates on packing list. ** indicates on the IGI grading report.

3. Optical Microscopy

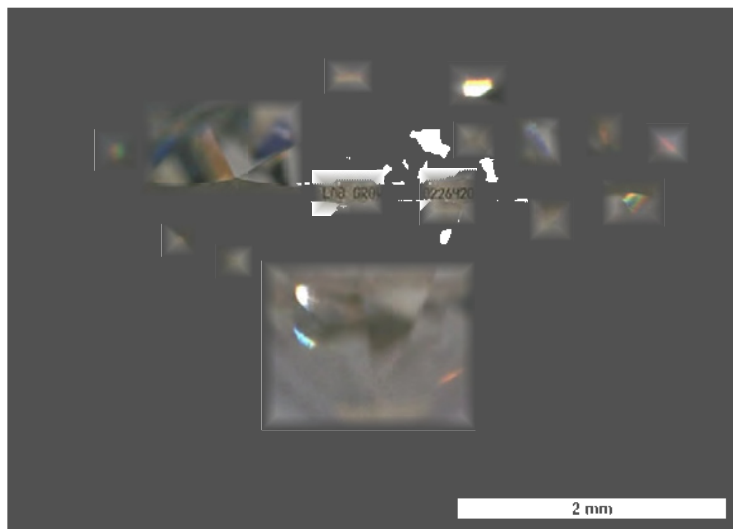


Figure 4: An image of NL702 showing the laser inscription on the girdle: Lab Grown LG10226420

4. DiamondSure and DiamondPLus testing

NL702 was tested using DiamondSure and DiamondPLus. The results are given below in Table 2 and indicate that the stone is a CVD synthetic diamond.

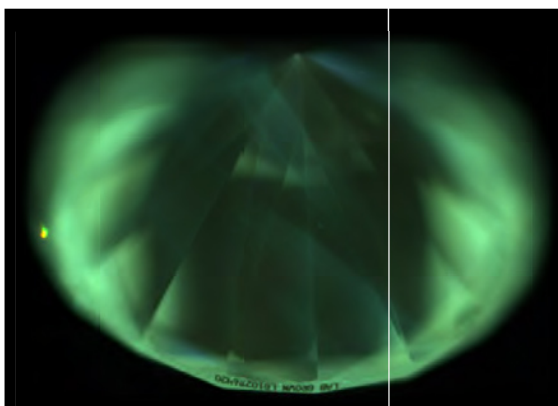
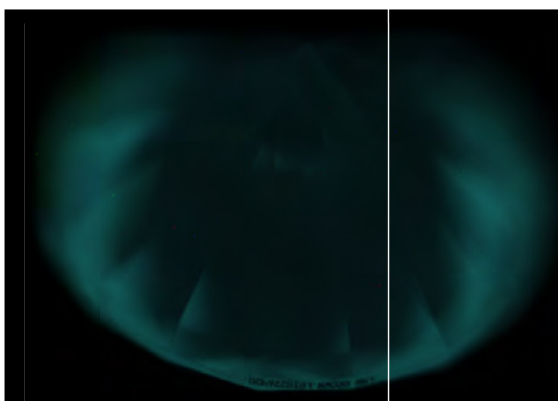
Gemstone	DiamondSure results	DiamondPLUS results
NL702	'Refer for further tests (Type II)'	'Refer (CVD synthetic?)'

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Table 2: DiamondSure and DiamondPLus results for NL702**5. DiamondView and Photoluminescence Spectroscopy**

Surface fluorescence images and phosphorescence images of NL702 were recorded using DiamondView. Figure 5 shows one of the images recorded. The girdle inscription is clearly visible. The dominant fluorescence colour is green and striations that are typically of CVD synthetic diamond are visible. Figure 6 shows a phosphorescence image of the sample. The combination of green fluorescence and blue phosphorescence has been observed in many Gemesis samples that we have previously studied and is often seen for nitrogen doped CVD synthetic diamond that has been heat treated (annealed) to improve its colour.

**Figure 5:** Fluorescence image of NL702 recorded using a DiamondView**Figure 6:** Phosphorescence image of NL702 recorded using a DiamondView

Photoluminescence spectra of NL702 were recorded at 77 K with different laser excitations. With 514 nm excitation, a line at 737 nm was readily detected and nitrogen vacancy defects with zero phonon lines at 575 nm and 637 nm were also detected with Raman normalised intensities of 0.22 and 0.23 respectively. With excitation at 458 nm, a line at 503 nm with a Raman normalised intensity of 0.44 indicated the presence of H3 defects (comprising two nitrogen atoms and a vacancy). The detection of H3 defects in material with such a low overall nitrogen content is supporting evidence that the sample has been annealed (heat treated) after growth.

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6. Processing into a parallel sided plate

NL702 was processed to produce a parallel sided plate for birefringence analysis. Figure 7 shows a series of images of the stone recorded at different stages of the processing into a parallel-side plate with thickness 0.71 mm and weight 0.18 ct. The stone was first laser sawn across its pavilion and the resulting surface and the table were then polished to enlarge the parallel-sided area of the sample available for birefringence analysis, leaving the girdle in the centre of the finished plate. After processing, the very shallow laser inscription was just visible (see Figure 8).

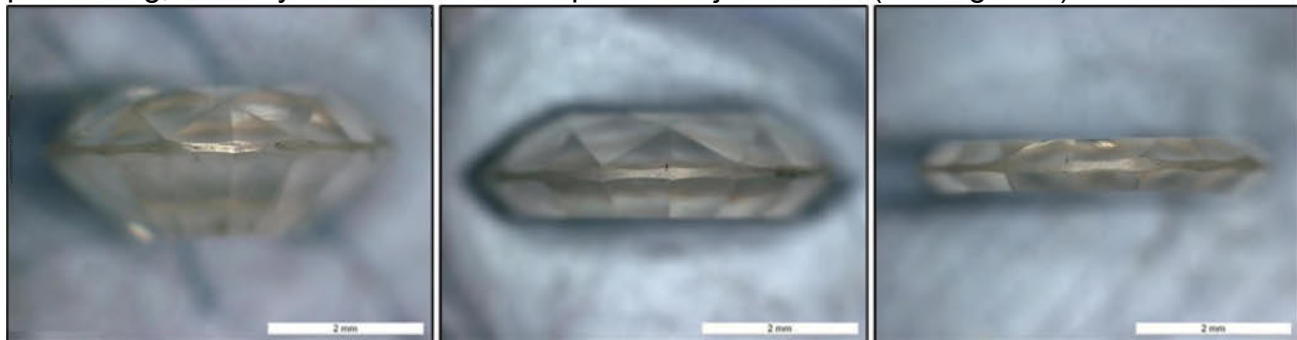


Figure 7: Images of NL702 recorded at different stages of processing into a parallel-side plate with thickness 0.71 mm and weight 0.18 ct.

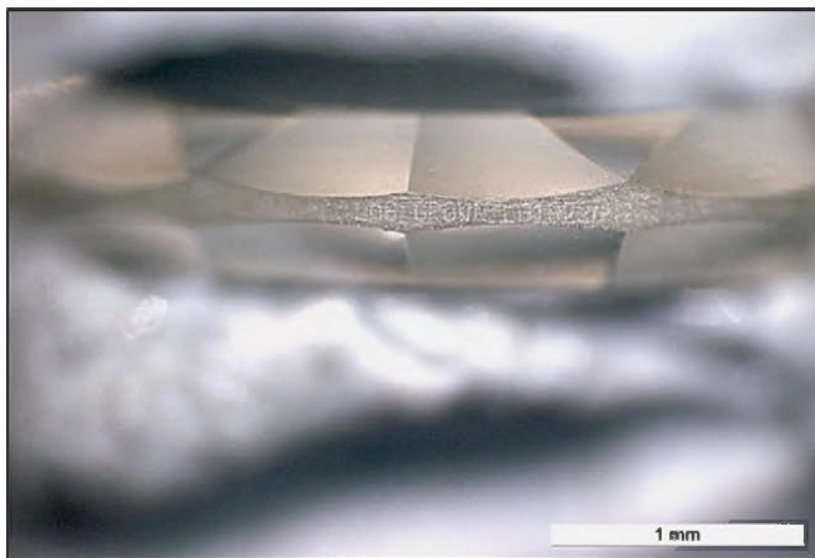


Figure 8: After processing, the very shallow laser inscription was just visible.

7. NL702: Metripol Analysis of Optical Quality

The parallel-sided plate (with a thickness of 0.71 mm, a diameter of 4.56 mm) produced from NL702 was imaged using a Metripol microscope at Warwick University using an illumination wavelength of 590 nm to give $\sin \delta$ values pixel-by-pixel. Nineteen overlapping images of the sample were collected using a 4x objective, which provides a 1360 x 1024 pixel image covering 1.581 x 1.191 mm area (approximate pixel size of 1.163 x 1.163 μm). For each sample the overlapping images were then stitched together to create an image of the entire area of the sample. The image stitching was completed using the free program 'ImageJ' with the 'stitching' plugin. This program allows the user to manually place individual image frames into position. The frame positions can then be computationally optimised and a stitched image / mosaic is generated along with a text file containing the optimized frame positions. De Beers Technologies UK have used a Matlab script, to stitch .ssf (data) files into an image using the optimized frame positions. A Matlab script has also been used to select and analyse appropriate rectangular, or circular regions of interest from the .ssf data image.

A $\sin \delta$ image and histogram for a selected region of sample NL702 are shown in Figure 9.

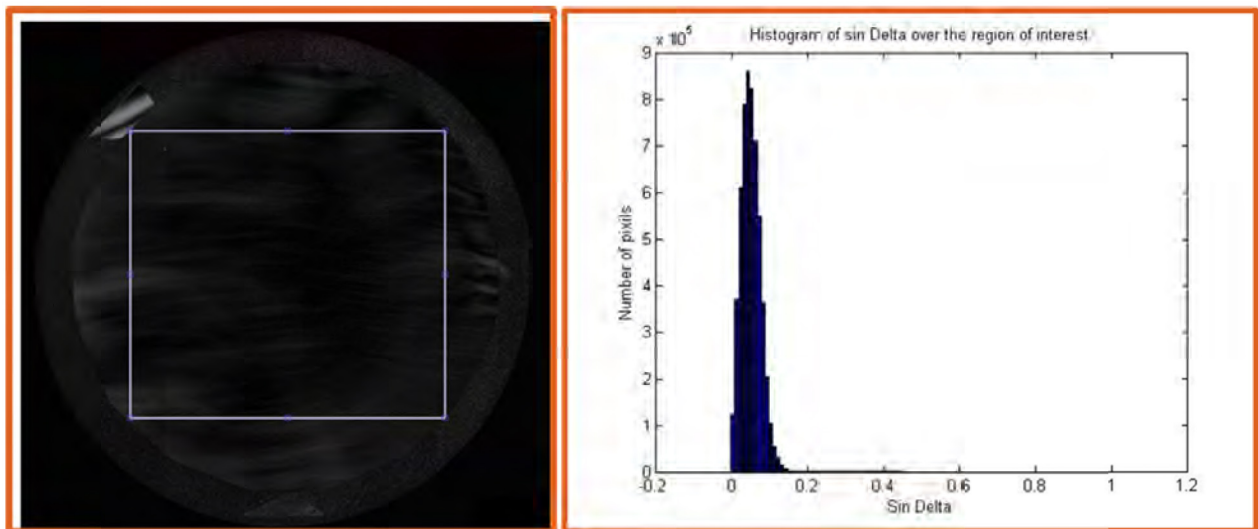


Figure 9: $\sin \delta$ Metripol image of the entire area of NL702 and a histogram of the $\sin \delta$ values for the region of the sample indicated by the white box in the Metripol image.

Two square regions of the sample image were selected as illustrated in Figure 10. These areas had dimensions of 1.3 mm x 1.3 mm and 2.5 mm x 2.5 mm.

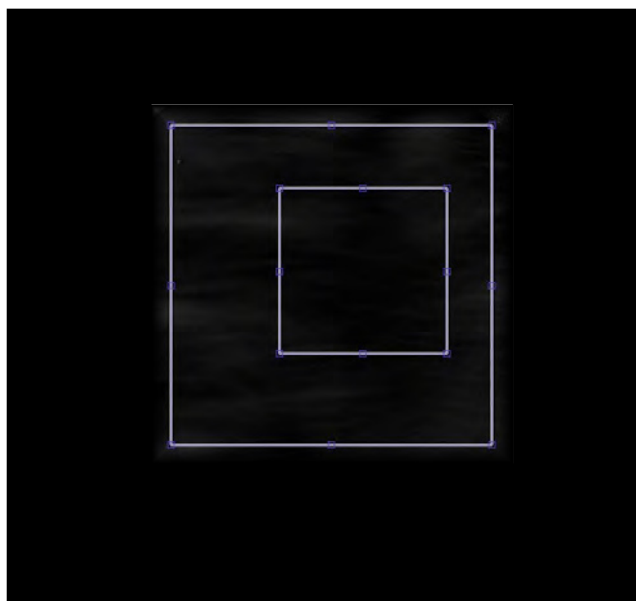


Figure 10: A Sin δ Metripol image of NL702 showing square regions of the sample selected for analysis of the distribution of sin δ values. The dimensions of these regions were 1.3 mm x 1.3 mm and 2.5 mm x 2.5 mm.

For the two selected areas the maximum sin δ value was found (sin δ_{\max}), and hence δ_{\max} was calculated. Using the equation $\Delta n_{\max} = \delta_{\max} \lambda_{\text{meas}} / 2\pi L$, Δn_{\max} was then deduced. The results for NL702 are given in Table 3. This table also includes sin δ_{\max} and Δn_{\max} values after selection of the pixels with the 99% and 98% lowest values. Consideration of possible sources of measurement error indicates that the measured sin δ_{\max} values are within 0.02 of the true values and the Δn_{\max} values are within 3×10^{-6} of the true values.

Dimension of selected area (mm)	Sin δ_{\max} (for 100% of the analysed area)	Δn_{\max} (for 100% of the analysed area)	Sin δ_{\max} (for 99% of the analysed area)	Δn_{\max} (for 99% of the analysed area)	Sin δ_{\max} (for 98% of the analysed area)	Δn_{\max} (for 98% of the analysed area)
1.3 x 1.3	0.141	1.87×10^{-5}	0.085	1.13×10^{-5}	0.080	1.06×10^{-5}
2.5 x 2.5	0.447	6.13×10^{-5}	0.106	1.40×10^{-5}	0.101	1.34×10^{-5}

Table 3: sin δ_{\max} and Δn_{\max} values for selected regions the NL702 plate shown in figure 10. Values are given for 100% of the analysed area and for 99% and 98% of the analysed area.

8. Electron Paramagnetic Resonance (EPR)

The N_s^0 concentration for the parallel-sided plate was measured at Warwick University using rapid passage EPR and found to be 460(40) ppb ($8.1 \times 10^{16} \text{ cm}^{-3}$).

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9. Fourier Transform Infrared (FTIR) Spectroscopy

An FTIR spectrum was recorded for the round brilliant at 0.5 cm^{-1} resolution. The integrated absorption coefficient for the line in the spectrum at 1344 cm^{-1} indicated an N_s^0 concentration of 0.5 ppm, in good agreement with the concentration deduced from EPR. From the strength of the line at 1331 cm^{-1} the upper limited for the N_s^+ concentration was found to be 0.1 ppm. No line was detected at 3123 cm^{-1} and therefore the concentration of NVH^0 was below the detection limit. The spectrum did however contain a weak line at 1341 cm^{-1} that we have previously only observed for CVD synthetic diamond that has been exposed to heat treatment that has removed or reduced brown colour.

10. Measurement of Near-Infrared Absorption Coefficient

The parallel-side plate produced from NL702 was sent to Laser Zentrum Hannover for laser calorimetry measurements of absorbance at 1064 nm (1.064 μm). The method followed ISO 11551:2003 and gave an absorbance result for the plate of 3131 ppm (3131×10^{-6}). From this result and the thickness of the plate (0.71 mm) an absorption coefficient at 1064 nm of 0.044(5) cm^{-1} was deduced. More details of the measurement are given in an LZH optics characterisation measurement report (#Report-14846.pdf) dated 30 March 2016.

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TECHNICAL REPORT

Summary of Evidence that NL702 had been Heat Treated (Annealed) after Growth

1. Introduction

NL702, a round brilliant polished gemstone of 0.38 ct weight, was received from Ayako Lawson at De Beers Technologies UK in late 2015. After preliminary characterization it was processed to produce a parallel-side plate for birefringence investigation and for measurement of the NIR absorbance. This short report presents key findings of the characterization that provide evidence that the material had been annealed after growth.

2. Absorption spectroscopy

The EPR spectrum of the parallel sided plate produced from NL702 was measured at Warwick University and indicated that the concentration of neutral single nitrogen was 460(40) ppb.

The FTIR absorption spectrum shows very little extrinsic absorption small absorption peaks at 1332, 1344 and 1341 cm^{-1} . The integrated absorption coefficient of the feature at 1344 indicated a single substitutional nitrogen concentration of approximately 0.5 ppm, consistent with the EPR measurement. The integrated absorption coefficient for the feature at 1332 cm^{-1} indicated a maximum concentration of positively charged single nitrogen of approximately 0.1 ppm. In our experience the feature at 1341 cm^{-1} has only been observed for samples that have been annealed at high temperature after growth. No absorption feature was observed at 3123 cm^{-1} . As-grown nitrogen containing CVD synthetic diamond tends to show an absorption feature at 3123 cm^{-1} which removed by post-growth annealing at high temperature.

These results indicate that nitrogen is an impurity in NL702 and together they indicate that the sample was annealed after growth.

3. Photoluminescence spectroscopy

Photoluminescence spectra from NL702 were recorded at liquid nitrogen temperature (77 K) for various excitation wavelengths and some of the key photoluminescence lines observed are listed in table 1.

Excitation wavelength (nm)	PL features (nm) shown by NL702	Notes
325	N3: 415.1 nm, 427.7 nm, H3: 503.1 nm	Lines not seen in as-grown material
458	H3: 503 nm	$I(\text{H3})/I(\text{Raman}) = 0.44$
488	H3: 503 nm	H3 consistent with heat treatment
514	540.5 nm, NV^0 : 575 nm, NV^- : 637 nm, 737 nm	$I(\text{NV}^0) \text{ ZPL and } I(\text{NV}^-) \text{ ZPL} \approx 0.22\text{-}0.23 \times \text{Raman}$, Observation of 540.5 nm PL suggests annealing. $I(737)/I(\text{Raman}) = 0.007$

Table 1 Key zero phonon lines (ZPL) present in photoluminescence spectra of NL702 recorded at liquid nitrogen temperature with various different laser excitation wavelengths

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Table 2 lists Raman normalized intensities for some zero phonon lines present in photoluminescence spectra of NL702, along with other intensity ratios derived from the measurements.

$I(\text{NV}^0 \text{ ZPL})/I(\text{Raman})$	0.22
$I(\text{NV}^- \text{ ZPL})/I(\text{Raman})$	0.23
$I(\text{NV}^- \text{ ZPL})/I(\text{NV}^0 \text{ ZPL})$	0.45
$I(\text{H3 ZPL})/I(\text{Raman})$ (458 nm excitation)	0.44
$I(\text{H3 ZPL})/I(\text{NV}_{\text{total}})$ where $I(\text{NV}_{\text{total}}) = I(\text{NV}^0 \text{ ZPL}) + I(\text{NV}^- \text{ ZPL})$	0.982

Table 2 Raman normalized zero phonon line (ZPL) intensities for various defect centres

Previous investigations of the effect of heat treatment on the properties of CVD synthetic diamond samples produced by Element Six for research purposes have indicated that the ratio of the intensity of the H3 zero phonon line to the summed intensities of the NV^0 and NV^- zero phonon lines is changed by post-growth heat treatment (sometimes called annealing) in the way shown in figure 1. It can be seen from this figure that there is a marked increase of the ratio as a function of annealing temperature and measurements on a range of different samples have indicated that the ratio can be used as a reliable indicator of whether or not a sample has been post-growth heat treated and the approximate temperature of such heat treatment. The value of the ratio measured for NL702 is shown by the blue line in figure 1 and indicates an equivalent four hour heat treatment temperature of between 1900 and 2300°C.

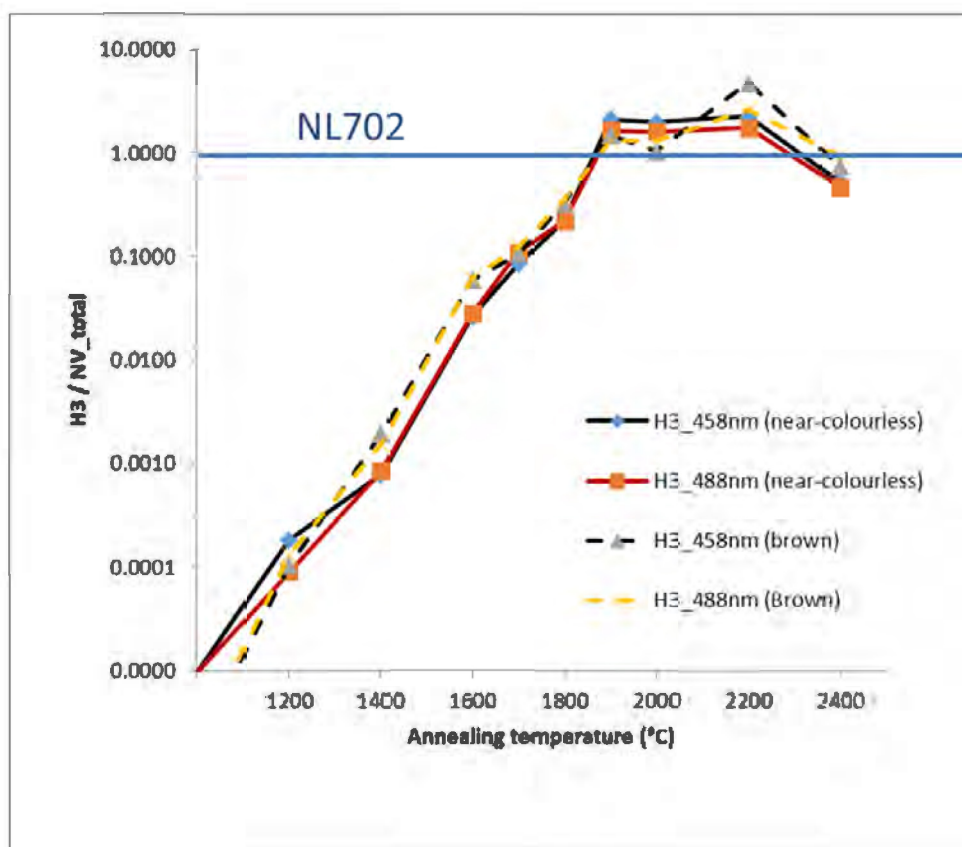


Figure 1 The ratio of H3/NV fluorescence intensities as a function of annealing temperature for brown and near-colourless CVD synthetic diamond. Results are shown for two different excitation wavelengths: 458 nm and 488 nm. The ratio for NL702 is shown by the horizontal line and suggests an equivalent four hour heat treatment temperature in the approximate range 1900-2300°C.

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4. DiamondView images

In DiamondView samples are illuminated with above bandgap radiation and images are then captured of the resulting surface fluorescence and phosphorescence. The instrument is used by the diamond trade (eg grading laboratories) for identification of natural and synthetic diamond. It is also a useful sample characterization tool for research into the effects of heat treatment of synthetic diamond and in the course of such research carried out at De Beers Technologies we have captured images of CVD synthetic diamond samples of various kinds in their as-grown form and after heat treatments at different temperatures. **Figure 2** shows a series of DiamondView images of CVD synthetic diamond samples annealed at successively higher temperatures.

	<i>Microscopy Initial</i>	<i>DiamondView Initial</i>	<i>Microscopy T1</i>	<i>DiamondView T1</i>	<i>DiamondView (phosph.) T1</i>
1200°C / 4h DTC					none
1400°C / 4h DTC					none
1600°C / 4h IaM					none
1700°C / 4h IaM					
1800°C / 4h IaM					
1900°C / 4h IaM					
2000°C / 4h IaM					
2200°C / 4h IaM					
2400°C / 4h IaM					

Figure 2 Microscopy and DiamondView images of CVD synthetic diamond samples heat treated at different temperatures. The 1200 and 1400°C treatments were carried out at atmospheric pressure but the other heat treatments were carried out with diamond stabilizing pressure.

It can be seen from figure 2 that as the temperature of the heat treatment applied to brown CVD synthetic diamond is increased

- i) the brown colour is removed,
- ii) the dominant fluorescence colour changes from orange to green and then to blue
- iii) green phosphorescence appears and then, at higher temperatures, the dominant colour of the phosphorescence changes from green to blue.

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DiamondView images of NL702 are shown below in figure 3 (fluorescence) and figure 4 (phosphorescence). The fluorescence images show striations that indicate that can be used to identify that the material is CVD synthetic diamond. The dominant colour of the fluorescence and together with the observation of blue phosphorescence is not consistent with what is observed for as-grown nitrogen-doped CVD diamond but is consistent with what would be expected for nitrogen-doped CVD synthetic diamond material that has been heat treated at high temperatures as illustrated in figure 1. Matching of the fluorescence/phosphorescence colours suggests an equivalent four hour heat treatment temperature in the approximate range 2000-2200°C in agreement with the range indicated by the photoluminescence intensity ratio method outlined in section 3.

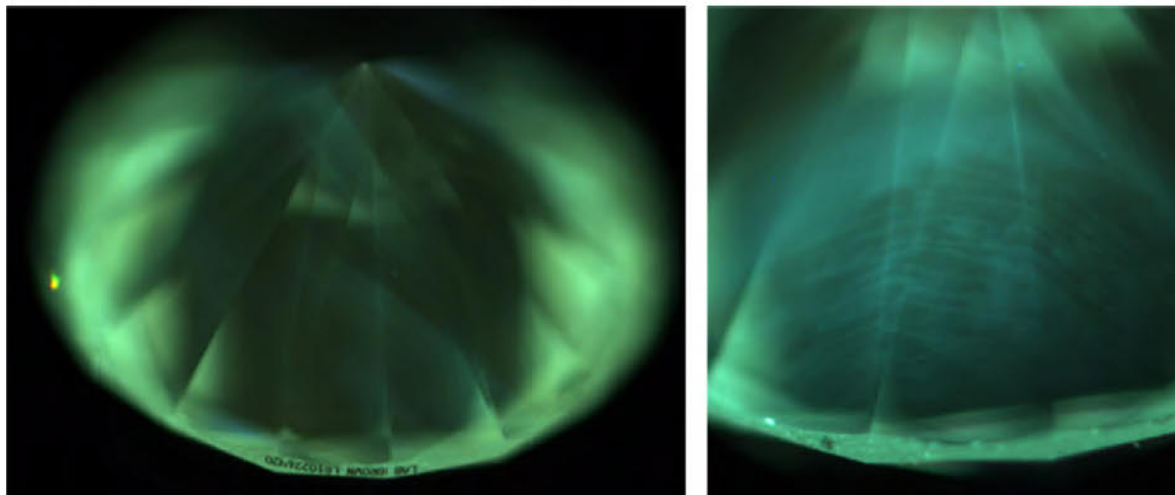


Figure 3 DiamondView fluorescence images of NL702



Figure 4 DiamondView phosphorescence images of NL702

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5. Summary of characteristics of optical grade CVD synthetic diamond plates sold by Microwave Enterprises and changes observed after heat treatment

As detailed in this short report, characterization of the CVD synthetic diamond sample NL702 bought from Pure Grown Diamonds has strongly indicated that it has been heat treated after growth. We have, however, also had the opportunity to study ten CVD synthetic diamond plates (NL625-1 to -10) sold by Microwave Enterprises for optical applications and stated by them to have been produced by Ila Technologies and we found these samples to have characteristics consistent with their not having been heat treated after growth. This gave us the opportunity to investigate the effect of heat treatment on material grown by Ila Technologies. NL625-01 was heat treated at 2100°C for 30 minutes and NL625-06 was heat treated at 2400°C for 30 minutes. The effect on the fluorescence and phosphorescence characteristics is illustrated in figure 5.

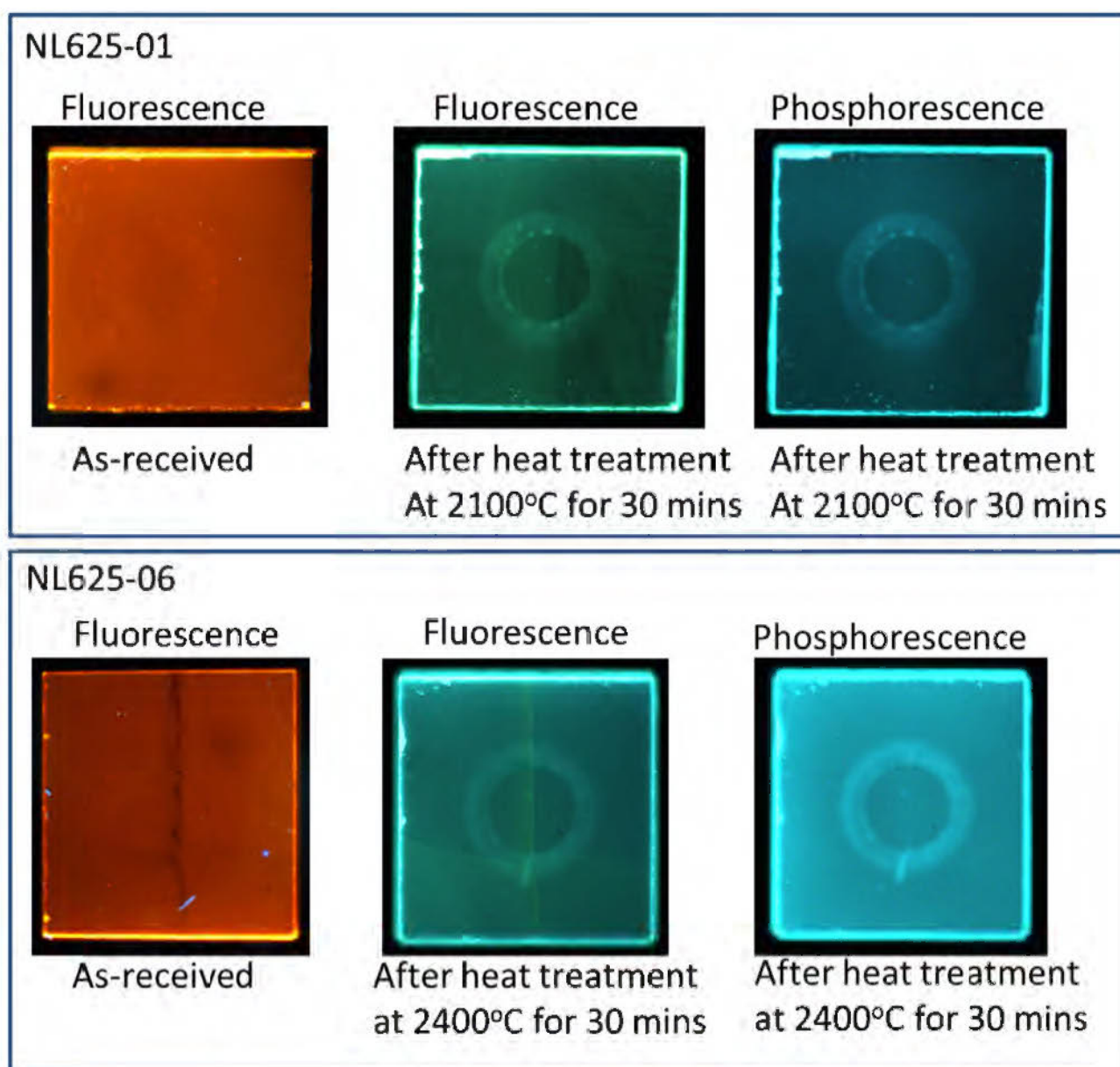


Figure 5 DiamondView images of NL625-01 and NL615-06 before and after heat treatment. Neither sample showed phosphorescence in their as-received form.

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Photoluminescence spectra of all ten of the samples NL625-01 to -10 in their as-received form showed strong 575 and 637 nm lines from NV defects (with 514 nm excitation) and no H3 luminescence (with either 488 nm or 458 nm excitation). Although they were stated to be for optical applications they were brown and their UV/visible absorption spectra showed the gradual rise in absorption towards shorter wavelengths that is typical of as-grown nitrogen-doped CVD synthetic diamond samples. EPR spectroscopy indicated that they contained between 0.063 and 0.225 ppm of single substitutional nitrogen (NL625-01: 0.225 ppm and NL625-06: 0.100 ppm).

Detailed photoluminescence spectroscopy of the heat treated samples has not been carried out but comparison of figures 2 and 5 shows that the heat treated samples have DiamondView fluorescence and phosphorescence characteristics very similar to those of samples that we had previously grown and heat treated in the same temperature range as part of our experimental programme. Comparison of figure 5 with figures 3 and 4 shows that the DiamondView fluorescence and phosphorescence characteristics of NL702 are very similar to those of the two NL625 samples that we heat treated at high temperatures.

6. Discussion

CVD diamond grown with nitrogen present in the growth environment tends to be brown and to contain nitrogen in forms such as single substitutional nitrogen, nitrogen-vacancy (NV) centres and nitrogen vacancy hydrogen (NVH) centres. Single substitutional nitrogen gives rise to the absorption feature at 270 nm and the P1 lines in the EPR spectrum. NV defects give rise to 575 and 637 nm luminescence features observed when a sample is excited at 514 nm, for example. NVH defects are responsible for the 3123 cm^{-1} line in the FTIR spectrum and a band at about 520 nm in the visible absorption spectrum.

When such CVD diamond is heat treated at high temperatures NVH defects are dissociated and as a result the 3123 cm^{-1} line and the 520 nm band are no longer observed. NV centres dissociate but low concentrations of these defects remain because of a dynamic equilibrium between their formation and loss. As a result the NV fluorescence intensity is reduced but weaker NV luminescence is still observable for nitrogen containing heat treated CVD diamond. Single substitutional nitrogen remains after heat treatment and in addition some nitrogen is found in an aggregated form known as the H3 centre. This is made up of two nitrogen atoms with a neighbouring missing carbon atom (vacancy). Our research has shown that as nitrogen containing CVD diamond is heat treated at successively higher temperatures, for given excitation conditions the ratio of the H3 luminescence intensity to the NV luminescence intensity increases in a way that enables the approximate temperature of heat treatment to be deduced from measurement of this ratio. For as-grown samples the H3 fluorescence is generally absent and NV fluorescence is strong.

The effect of heat treatment on defect centres responsible for fluorescence (NV centres and H3) also helps to explain the changes in the colours of the fluorescence observed in DiamondView images when samples are heat treated. Heat treatment reduces the concentration of NV centres that show orange/red fluorescence and increases the intensity of H3 centres that show green fluorescence. Additional blue fluorescence is introduced when samples are annealed at the highest temperatures.

For NL702 the results of absorption spectroscopy are consistent with heat treatment because of the absence of absorption from defects that are typically grown into CVD diamond but would be

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removed by heat treatment and the presence of the 1341 cm^{-1} line that we have only observed for annealed CVD synthetic diamond. The results of photoluminescence spectroscopy and DiamondView imaging provide strong evidence that NL702 has been heat treated and indicate an equivalent four hour heat treatment in the approximate range $1900\text{-}2300^{\circ}\text{C}$.

Samples received from Microwave Enterprises had characteristics consistent with their being in their as-grown form. When two of these samples were heat treated at 2100°C and 2400°C for 30 minutes, after the heat treatment their DiamondView characteristics were very similar to those of NL702. This indicates that when material believed to have been produced by Ila Technologies is heat treated at high temperatures its DiamondView characteristics change dramatically from orange fluorescence and no phosphorescence to blue/green fluorescence and blue phosphorescence. NL702 showed blue/green fluorescence and blue phosphorescence and this is therefore additional evidence that it had been heat treated at high temperatures.

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